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By W. CRAWFORD † and D. B. COX ‡

SUMMARY

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Side effects due to fluid polymerization are defined by the use of lubricating fluids of differing radiation stabilities, each thickener being used in conjunction with an alkyl phenyl silicone, a refined petroleum bright stock, and/or a synthetic aromatic, respectively.

Additives are described which act as "energy absorbers" or "free radical scavengers." These materials, "antirads," are shown to boost the radiation stability of a modified clay/silicone fluid grease by up to 1000 megarads.

Facilities for the simultaneous irradiation and bearing rig testing of greases are described.

It is shown that the interaction of grease composition, method of test irradiation, and method of damage evaluation is complex, and that development of radiation-resistant greases for different environments requires understanding of this interaction.

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In the design of U.K. power reactors, stress has been laid in adapting, where possible, well-tried engineering principles. This has applied not only to the many novel handling devices involved but also to their lubrication. Thus, although recourse has been made to dry lubrication [1, 2] and the use of layer lattice solids for applications beyond the scope of existing lubricating fluids and greases, there exists a demand to extend the range of the latter products in respect of their resistance to both ionizing radiation and sustained high temperatures.

A survey of the performance levels required of greases for control rod actuating mechanisms, fuelling machines, and ancillary equipment is given in Table I. In addition to thermal and radiation stability, other requirements include low volatility and compatibility with the materials and atmosphere of the reactor.

Conventional soap-thickened greases lose structure at radiation dosages as low as 50–300 megarads, and few can be used for extended periods at temperatures above 120° C. They are, moreover, subject to degragradation in pressurized carbon dioxide atmospheres. To meet the more exacting requirements of nuclear power plant lubrication, attention must therefore be focused on non-soap thickeners and on lubricating fluids of superior radiation resistance and oxidation stability. Realistic targets for greases so compounded are:

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Since lubricating fluids are known which retain their lubricity and oxidation stability to dosages as high as 3000 megarads and can withstand 250° C, the main limitations in the development of a grease for use in radioactive environments would appear to be related to the choice of thickener. This paper is thus partly concerned with factors influencing thickener selection and with thickener–fluid interaction. Data on the radiation stability of 17 thickener–fluid systems are included.

Another factor in evaluating radiation-resistant greases is whether the irradiation is done on cool, static grease or on hot grease being sheared in a bearing. It will be shown that strikingly different results have been obtained with change in these variables.

A third factor of importance is the test by which radiation damage is assessed. Again, it has been shown that different tests will give widely varying evaluations of the same grease sample. The interaction of these three factors must be considered.

Finally, it will be shown that it is possible to make

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high performance products out of otherwise unsuitable grease by means of certain additives, called "antirads." The various types of antirads, the mechanisms by which they operate, and their effect on the performance of a grease of low radiation stability are reviewed.

down under shear, and the Shell roll stability apparatus used in the present work is much favoured. However, when dealing with non-soap greases, which normally rely on mechanical as opposed to thermal dispersion for their production, the results of tests in which the grease is subjected to shearing influences

TABLE I

Anticipated Typical Operating Conditions in Components of CO_2 Cooled, Graphite Moderated Reactors

Component	Operating temperature, °C	Radiation dosage, rads/year	Operating atmosphere	Maintenance interval
CO_2 Gas Valves				
Gears, bearings, and hydraulics	70–150 or higher	10^3	Air at atmospheric or slight pressure	2 years
Control Rod Mechanisms				
Gears and bearings	70–150	10^3 to 5×10^5	CO_2 at 150–300 psi	2–5 years, depending on design
Fuelling Machines				
(*a*) Bearings and gears	100–400	10^3 to 3×10^9	CO_2 and air from partial vacuum to 150–300 psi	6–9 months where radiation and temperature conditions are severe
(*b*) Cooling fan bearing	100 max	10^3 max	CO_2 and air from 150–300 psi	
Ancillary Machines				
1. *Service Machines* (when separate from fuelling machine) Gears and bearings	70–100	10^5 max under normal conditions	CO_2 from partial vacuum to 150–300 psi	12 months
2. *Charge Chute Machines* (when separate from fuelling machine) Gears and bearings	100–400	10^6–10^8	CO_2 from atmospheric pressure up to 150–300 psi	12 months
3. *Reactor Observation Equipment* (when separate from fuelling machine)	100 max	Dependent on use but could be high	CO_2 and air from atmospheric pressure up to 150–300 psi	12 months
Spent Fuel Element Conveyor Systems Chains and bearings	100 max	2×10^8 max under normal conditions	Air at atmospheric pressure	12 months

TEST METHODS

In the present work a number of test procedures were employed to assess radiation damage, and some discussion of their interpretation is merited.

Penetration Measurements

Taken in themselves, consistency changes can be misleading, since polymerization of the fluid phase can balance structural breakdown of the thickener and thus give an optimistic estimate of the radiation stability of a grease. Since changes in the two phases proceed simultaneously, the graph of consistency change *v.* applied radiation dose can take a number of different forms up to the point where polymerization of the fluid and thickener degeneration products predominates, a progressive stiffening occurring thereafter. A penetration change relating to a single predetermined radiation level has therefore little meaning.

Mechanical Stability Tests

A number of procedures are widely accepted for measuring the resistance of grease to structural breakmust be treated with reserve. Thus it has been demonstrated that if a modified bentonite clay, a mineral oil, and a suitable dispersant are charged to a Shell roll stability apparatus and rolled for three hours at 200° F, an excellent grease structure is produced. In the same way it is believed that radiation damage can be "repaired" in some cases by mechanical working. This, of course, has implications when considering the anomalies that exist between the results of dynamic and static irradiation tests.

Bearing Rigs

Rigs employing loaded anti-friction bearings are probably the most reliable tools available to the grease technologist in that they simulate service conditions most closely. When dealing with radiation-resistant greases, the grease can be rig tested after a period of static irradiation, or alternatively, the irradiation can be applied to the grease whilst the rig is operating.

It should not be expected that similar results will be obtained by the two different bearing test methods. It has been found in the authors' experience that two

greases successfully lubricated anti-friction bearings at elevated temperature whilst withstanding twice the radiation necessary to damage them very severely under static conditions and room temperature. Scarlett and Cliffe in a recent paper[3] noted a related phenomenon. With " in pile " dynamic testing, the bulk of the grease was cleared from the bearings prior to radiation damage, causing loss of mechanical stability. The same products, after static irradiation to lower levels, gave softening and leakage during the initial period of bearing clearance on subsequent dynamic testing. The same authors also highlighted the effects of " windage " or adequacy of sealing, which is a predominant factor with regard to the life of the lubricant in dynamic bearing tests.

There are several reasons which probably explain why some greases have been found more radiation resistant under dynamic bearing conditions.

1. Static irradiation is usually done at a temperature near 25° C, and any radical scavenger type oxidation inhibitor will be selectively destroyed before the grease is subjected to elevated temperature. If the grease depends markedly on the oxidation inhibitor for bearing performance, it will then perform very poorly in the bearing test.

2. It has been pointed out that shear can build up grease structure as well as break it down, depending, of course, on the composition and circumstance. It seems reasonable to suppose that with some greases the bearing shear of the dynamic irradiation test can help maintain structure and repair radiation damage, both by affecting the thickener dispersion and by minimizing fluid separation.

3. If radiation damage to the thickener depends on physical–chemical separation of molecular components, as has been suggested by Hotten and Carroll,[4] then it seems reasonable to suppose that elevated temperature would increase diffusion rates and molecular motion and favour re-combination of the separated fragments. (This is the obverse of radical " trapping " at low temperature.) Another possible contributing benefit of high temperature is the known fact that fluid viscosity rise for a given radiation dose is less the higher the temperature at which it is measured.

Other Tests

Fluid separation often occurs during static irradiation to an extent such as would presage leakage problems in service. Such separation, however, does not necessarily occur under dynamic conditions at a corresponding radiation dosage. It has further been found that some greases show reduced bleeding tendencies after static irradiation, due to fluid polymerization.

Oxidation stability is best assessed by dynamic bearing tests at elevated temperatures. Such tests, however, are limited by their long-term nature, and a useful indication of oxidation stability can be obtained by packing a 20-mm bearing (non-ferrous cage) with a fixed quantity of grease, placing the filled bearing on a watch glass in a convected, thermostatically controlled oven at, say, 150° C, and noting, by periodic inspection, changes in grease colour and structure, the extent of fluid separation, and the freedom of rotation of the bearing. In the present work, this test was used extensively for screening purposes, with recourse to dynamic bearing rig tests for confirmation of the more pertinent findings.

Radiation damage to greases is, in at least some cases, a thickener surface phenomenon, *i.e.* the grease may lose mechanical stability to 60 strokes working, even though no evidence of gross chemical change can be detected. In several instances it was found that the infra-red spectra of both the original and irradiated grease were essentially identical, even though the irradiated grease was unstable to working.

The Ferranti–Shirley cone-plate viscometer has been found to be a useful tool in the interpretation of radiation damage. This instrument, when modified to include automatically programmed shear rate patterns, can give quantitative data on grease response to a wide variety of shear conditions. It therefore overlaps information obtained from penetrations, worker tests, Shell roll tests, and other mechanical devices. Its advantage lies in its ability to separate and measure effects of yield value, shear-thinning as a function of shear rate, shear-thinning or thickening as a function of time, and so forth. Fig 1 shows flow curves for a grease at various levels of irradiation. It is seen that this grease, which had been statically irradiated, showed gross breakdown only at 1000 megarads. In contrast, the same grease showed severe loss of structure at 500 megarads when measured by 60-stroke penetration, but passed 1000 megarads in a cyclic bearing test at 120° C.

In the series of irradiations just described, the contribution of fluid viscosity increase was assessed by extracting the fluid phase and measuring its viscosity. Fig 2 shows that the fluid viscosity had risen to about four times its original value by 1000 megarads (measured at 100° F).

Dynamic Irradiation Tests

For the dynamic irradiation tests a special rig (SETRA) was constructed for operation in the Harwell spent fuel element, gamma facility (Fig 3). This rig employs four vertically mounted, 20-mm ball bearings, radially loaded to 100 lb and operating in a gamma flux of 1–3 megarads/hour at temperatures up to 250° C. A constantly changing atmosphere of carbon dioxide surrounds the test bearings, which are shielded by "Nilos" seals. A gear train is also incorporated to yield data under different shear conditions. A speed of 900 rev/min was adopted as being representative of the majority of $D_m n$ values encountered

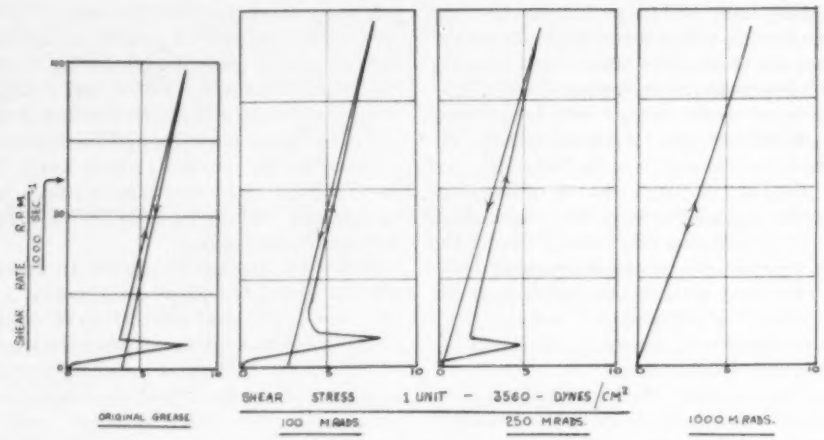

FIG 1

FLOW CURVES

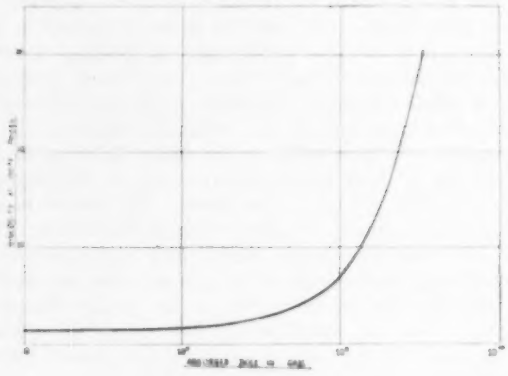

FIG 2

VISCOSITY OF EXTRACTED FLUID

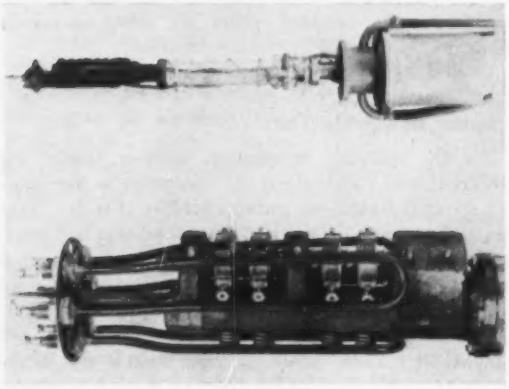

FIG 3

SETRA RIG

in the various fuelling machines, control rod mechanisms, and ancillary equipment. The lubricated components of these mechanisms are subjected to irradiation, which is predominantly gamma. The employment of a gamma facility for test work of this nature is thus realistic, besides offering advantages in terms of the handling of irradiated products and accurate dosimetry. In the latter context the difference between applied dose and received dose can be large. Even with gamma irradiation, a 40 per cent reduction was measured in certain locations within the rig due to interference by bearing housings, heat insulating materials, and the canister containing the rig.

Dosimetry

The method of dosimetry is to irradiate solutions of ferrous sulphate located at the bearing positions. The amount of chemical change is measured by spectrophotometric determination of the ferric ions formed, and this is used to calculate the doses received at the points of interest.

INFLUENCE OF THICKENERS

The selection of the thickener, or solid phase, of a lubricating grease designed for nuclear applications is limited by compatibility considerations and its resistance to damage by the separate or combined effects of radiation, high temperature operation, and mechanical shear.

Certain elements are undesirable constituents, since their accidental introduction into an atomic pile could seriously affect its economy or, alternatively, react with the fuel element canning material to give low melting point eutectics. Elements with high neutron cross-sections are thus debarred, as are also those that are incompatible with the particular canning material

employed. Accordingly, the UKAEA have imposed restrictions with regard to lubricant composition, and these are shown in Table II.

TABLE II

Restricted Elements in Lubricants for Reactors Employing Magnox Fuel Cans

Elements	Permissible amount
Mercury	None
Barium, bismuth, cadmium, gallium, indium, lead, lithium, sodium, thallium, tin, zinc	0·1%
Aluminium, antimony, calcium, cerium, copper, nickel, silver, strontium, praseodymium	1·0%

These limits may be exceeded where the metal is in a stable compounded form and satisfies compatibility tests.

The carbon dioxide cooled, graphite moderated reactor poses a special problem in that a pressurized carbon dioxide atmosphere can cause rapid degeneration of conventional soap thickened greases, presumably by carbonate formation. Other restrictions on the use of soap greases have prevented any exhaustive study of the mechanism of this degradation.

The character of the base fluid must also be considered in the selection of the thickener, since certain thickener/fluid combinations give, at best, weak gels that fluidize readily under shearing stresses. For example, the authors were unsuccessful in forming a satisfactory grease structure when attempting to thicken a paraffinic bright stock with an indanthrene pigment.

The thermal and oxidation stabilities of the basic grease constituents assume a new importance in greases subjected to ionizing radiation. One of the early symptoms of radiation damage is a drop in oxidation stability due to increasing unsaturation and free radical formation, and since the majority of conventional anti-oxidants have little resistance to radiation, they are " knocked out " in the early stages of grease deterioration before their efficient functioning is most required. As will be illustrated, thickeners vary in the extent to which radiation affects oxidation stability, and some are even claimed to be anti-oxidants in their own right.[5]

Assuming that the secondary requirements outlined above are met, there remains the question of the thickener's resistance to structural damage from radiation. Much has been reported in the literature [6–13] on the desirability of certain molecular configurations for imparting enhanced radiation resistance by the absorption of energy without accompanying bond fission. The same general rules probably apply to thickener systems, but whereas damage to lubricating fluids can be defined in terms of such relatively simple parameters as viscosity increase and gas evolution, thickener degeneration can be considerably more complex with either losses or apparent improvements in thickening power, shear stability, and fluid separation characteristics resulting from structural change.

Thickener Systems Investigated

A selection was made of some of the more promising thickeners that have been developed in the post-war years. These included a number of modified clays and silicas, dye pigments, a substituted aryl urea, and the metal salts of *n*-octadecyl terephthalic acid.

(1) *Modified Clays and Silicas.* Four representatives of this class were chosen. Included were " Bentone 34 "* and " Baragel,"* both formed by a cation exchange reaction between a montmorillonite clay and a quaternary ammonium salt. The resultant hydrocarbon layer on its surface renders the clay oleophilic, but a polar dispersant is necessary to achieve efficient thickening. Two finely-divided silicas were also examined. One of these, " EP93," is surface treated with a silicone to render it hydrophobic, whereas the other, "Estersil,"[14] is esterified with *n*-butyl alcohol.

(2) *Dye Pigments.* A number of dye pigments and toners have been utilized as grease thickeners.[5, 15] For the purposes of this study, Monolite Fast Blue 3RS (Indanthrone) was selected as representative of this group.

(3) *Substituted Aryl Ureas.* These wholly organic thickeners are characterized by the diamido-carbonyl linkage [16, 17] and can be formed *in situ* by the reaction of a di-*iso*cyanate with an aryl amine. In the preparation of the greases described herein, a pre-made concentrate in mineral oil marketed under the name of Amoco 0578 was used, the mineral oil being displaced by a low boiling solvent, which was subsequently removed from the system by heating.

(4) *Metal Salts of Octadecyl Terephthalic Acid.* In this group the sodium salt has been most employed,[18] but this was obviously not suitable for U.K. nuclear greases due to incompatibility considerations. Greases were formed via the methyl ester utilizing the magnesium and aluminium salts, and those based on the former are included in this study.

Lubricating Fluids

To eliminate secondary effects due to changes in the fluid phase, each of the above thickeners was used in conjunction with at least two lubricating fluids chosen from:

(*a*) an alkyl phenyl silicone (cS at 100° F = 220);

(*b*) a solvent-refined Middle East bright stock (cS at 100° F = 575, vi = 100);

(*c*) a poly alkyl diphenyl ether (cS at 100° F = 175)

No anti-oxidants or antirads were included in the formulations.

* Products of National Lead Company, 111 Broadway, New York 6, N.Y.

Static Irradiation Data

Greases compounded from the above thickener/fluid systems were statically irradiated in the Harwell spent fuel element, gamma irradiation facility to received dosages ranging from 50 to 1000 megarads. The irradiated greases were examined for consistency change, loss of mechanical stability, fluid separation, reduction in oxidation resistance, and, with selected greases, change in bearing rig performance level.

Rigs employed included the Annapolis rig, operating

TABLE III

Comparison of Grease Thickeners Based on Static Irradiation to 1000 Megarads

Grease	Gamma dosage, megarads						Criteria of radiation damage
	50	100	300	500	700	1000	
Alkyl phenyl silicone/ Bentone 34	*	*		†	‡		Unworked penetration—pronounced stiffening at 700 megarads Worked penetration—softened to 500 megarads, then stiffened Rig performance—impaired at 500 megarads Oxidation stability—reduced at 500 megarads
Aryl urea		†		†	‡		Unworked penetration—progressive softening to 700 megarads Worked penetration—softened to 500 megarads, then stiffened Mechanical stability—affected at 100 megarads Separation—heavy at 700 megarads Oxidation stability—seepage at 500 megarads
Magnesium *n*-octadecyl terephthalamate	*	†		†			Worked penetration—softened to 500 megarads Oxidation stability—affected at 100 megarads—(heavy seepage at 500 megarads)
Estersil	†	†		†‡	‡		Unworked penetration—pronounced stiffening at 500 megarads Worked penetration—softened to 100 megarads, then stiffened Oxidation stability—affected at 50 megarads
Indanthrone		†		‡			Unworked penetration—softened to 700 megarads Worked penetration—softened to 500 megarads, then stiffened Mechanical stability—seriously impaired at 500 megarads Oxidation stability—reduced at 500 megarads
Baragel		*		‡			Unworked penetration—softened to 500 megarads Worked penetration—softened to 500 megarads Mechanical stability—seriously impaired at 500 megarads Oxidation stability—marked fall-off at 100 megarads
Siliconized silica		‡					Worked penetration—excessively soft at 100 megarads Separation—appreciable at 100 megarads
Bright stock/ Bentone 34	*	*		†	†	‡	Worked penetration—maximum softening at 500 megarads Mechanical stability—impaired at 500 megarads; seriously affected at 1000 megarads Rig performance—life reduced 50% at 500 megarads—little further deterioration at 1000 megarads
Aryl urea		*		†	†		Unworked and worked penetrations—softening to 700 megarads Mechanical stability—impaired at 700 megarads Oxidation stability—impaired at 500 megarads Rig performance—at 700 megarads similar to Bentone thickened grease
Magnesium *n*-octadecyl terephthalamate	†‡	†			†		Fluid separation—high at 50 megarads, but reducing thereafter to 700 megarads Drop point—low at 50 megarads Oxidation stability—seepage at 100 megarads; seriously affected at 700 megarads
Estersil	*	†		†	‡		Unworked penetration—slight stiffening to 1000 megarads Worked penetration—softening at 500 megarads Mechanical stability—impaired at 100 megarads Oxidation stability—seriously affected at 500 megarads
Baragel		†		†	‡		Unworked and worked penetrations—maximum softening at 500 megarads Mechanical stability—impaired at 100 megarads Drop point—low at 500 megarads; very low at 700 megarads Fluid separation—50% at 700 megarads Oxidation stability—impaired at 100 megarads

TABLE III—*Continued*

Grease	Gamma dosage, megarads						Criteria of Radiation Damage
	50	100	300	500	700	1000	
Polyalkyl diphenyl ether/ Bentone 34				†	†	†	Unworked penetration—softened at 700 megarads Worked penetration—softened at 500 megarads Drop point—some lowering at 1000 megarads Oxidation stability—impaired at 500 megarads—50% original at 1000 megarads
Aryl urea		*		†	†	†	Worked penetration—progressive softening to 1000 megarads Drop point—slight lowering at 1000 megarads Oxidation stability—impaired at 700 megarads Rig performance—at 700 megarads gave twice the life of corresponding Bentone 34 grease
Indanthrone				†	†	†	Unworked and worked penetrations—progressive softening to 1000 megarads Mechanical stability—impaired at 700 megarads Oxidation stability—70% original at 1000 megarads
Magnesium *n*-octadecyl terephthalamate		*		†	†	†	Unworked penetration—softened at 500 megarads Worked penetration—progressive softening to 1000 megarads
Siliconized silica		‡					Unworked penetration—softened excessively at 300 megarads Worked penetration—softened excessively at 100 megarads Fluid separation—severe at 100 megarads

* No appreciable damage. † Moderate damage impairing one or two aspects of performance. ‡ Severe damage.

at 5000 rev/min and at temperatures up to 163° C in a non-pressurized carbon dioxide atmosphere. A constant flow of gas was maintained during the tests, and other conditions, such as loading, shielding, and intermittent running schedule, were those that are standard for this rig.

The IP rig (IP 168/59T) was also employed. Test conditions were: speed—2500 rev/min; load—600 lb radial; temperature—120°–250° C; air atmosphere—normal shielding.

The results were analysed in terms of changes corresponding to moderate or severe radiation damage, and are summarized on this basis in Table III.

Where any particular grease property contributed to the assessment of radiation damage this is detailed in the final column. Where no reference is made, it can be assumed that the results showed no significant change or that the test data had little meaning. In the latter context, changes in drop point could be attributed to corresponding changes in consistency; roll stability tests on irradiated greases were rendered meaningless by viscosity increase of the base fluid or reformation of structure by shearing action; measurement of oxidation stability by static bearing tests was complicated by fluid separation and hardening effects resulting from radiation damage.

There were a number of instances where greases that were severely damaged at low radiation dosages showed little structural change at considerably higher dosages, due presumably to the balancing effects of fluid polymerization or structural change.

With the alkyl phenyl silicone fluid it was very noticeable that fluid polymerization was retarded by a number of thickeners—notably indanthrone and the aryl urea (Fig 4). This suggests a preferential absorption of energy by these materials. The accompanying

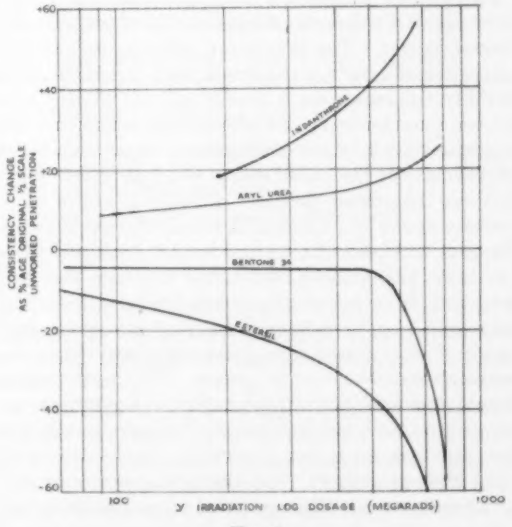

FIG 4

EFFECT OF THICKENER ON FLUID POLYMERIZATION

loss of thickening power was more noticeable with indanthrone. A surprising difference was that between Bentone 34 and Baragel, the former maintaining a mechanically stable grease structure to an appreciably higher radiation level. Structure recovery at

high radiation levels was a feature of the siliconized silica grease. For example, at 700 megarads the siliconized silica grease had penetrations within two–three points of the unirradiated product, broke down to a lesser extent on rolling at 200° F, and showed a lower fluid separation tendency. Indanthrone showed the least change in oxidation stability, but performance was marred by excessive softening and poor mechanical stability in the 500–700 megarad zone. With Estersil; polymerization reactions appeared to commence at an earlier stage than with the other thickeners, the grease attaining a hard rubbery consistency by 700 megrads. Magnesium *n*-octadecyl terephthalamate was incompletely evaluated, but was reasonably promising up to 500 megarads with no sign of fluid polymerization.

Greases produced using a solvent-refined, Middle East bright stock gave a similar pattern to those containing the silicone fluid. The differences between Bentone 34 and Baragel were more marked, serious degradation of the latter occurring at 700 megarads, whilst the Bentone 34 grease was relatively undamaged at 1000 megarads. Fluid polymerization, as denoted by stiffening at higher dosages, was not apparent with the aryl urea grease. The magnesium *n*-octadecyl terephthalamate grease gave a complex behaviour, suggesting considerable damage at 50 megarads, but thereafter improved resistance to the 700-megarad level.

The greases prepared from a poly alkyl diphenyl ether gave further confirmation of the thickener characteristics. The siliconized silica again suffered severe loss of structure at a low dosage. A mechanical stability test on a sample irradiated to 1000 megarads showed some recovery in line with that noted with the siliconized silica/bright stock grease. Performance of the Bentone 34 thickened grease was high, considering that on theoretical grounds damage to the surface modifier could be expected at relatively low dosages. Whereas with the silicone and bright stock oils there was little performance difference between the aryl urea and Bentone 34 thickened products over the range of dosage investigated, the aryl urea/poly alkyl diphenyl ether grease was appreciably better than the corresponding Bentone 34 grease. The maintenance of oxidation stability at high radiation levels that had been noted with the indanthrone/silicone grease was also apparent using this dyestuff to thicken the poly alkyl diphenyl ether. The thickening power of indanthrone is poor, and preparation of greases from it is difficult. This suggests that indanthrone and related pigments could be used to greater advantage as radiation stable anti-oxidants rather than as primary thickeners.

All three greases made with magnesium *n*-octadecyl terephthalamate tended to soften progressively with increasing radiation dose. This trend had its effect on all other performance tests, and no conclusive estimate could be made of its value as a thickener for radiation-resistant greases.

In general, considering the three lubricating fluids involved, interference with grease properties due to fluid polymerization was a feature of the alkyl phenyl silicone, but was non-existent with the diphenyl ether. Thus, whereas the former highlighted the capacity of the thickener to protect the lubricating fluid, the latter gave a more direct comparison of the radiation resistance of the thickeners themselves.

INFLUENCE OF ANTIRADS

The mechanism of the changes that occur in the molecular structure of organic materials subjected to ionizing radiation is not fully understood, but the following sequence has been suggested:

1. Excitation of the molecule resulting in bond fission and the production of free radicals.
2. Propagation of bond fission by hydrogen free radicals to yield gaseous hydrogen and unsaturated molecules or further free radicals.
3. Combination of free radicals to give cross-linked polymers.

The radiation resistance of any molecular configuration is a function of the radiation energy that can be absorbed and subsequently dissipated without accompanying bond fission. Thus, conjugated cyclic structures are capable of absorbing energy to give "excited" molecules which are resonance stabilized. There are, of course, limits to the amount of energy that can be absorbed in this manner without rupture of the chemical bonds occurring.

To inhibit radiation damage to a susceptible material, additives (antirads) may be incorporated which, broadly speaking, fall into two groups.

Free Radical Scavengers

These materials, of which the dialkyl selenides are a well-known example, do not inhibit the initial bond fission, but can reduce olefin formation and chain propagation. Thus, in relation to irradiated greases, breakdown of the thickener structure may not be retarded to an appreciable degree, but benefits will accrue in respect of a reduced rate of fluid polymerization and improved oxidation stability resulting from the higher degree of saturation.

Energy Absorbers

In this category, condensed aromatics and other highly conjugated cyclic compounds are particularly valuable. Thus, such materials as decacyclene, perylene, dibenzpyrenes, polyterphenyls, and dihydropyrene can be used to impart radiation stability to greases. In general, the structures that permit the highest degree of resonance are the most effective antirads. Polycyclics in which the aromatic rings

are separated by alkylene groupings, or where the conjugation is otherwise interrupted, are thus less effective than condensed ring structures. The presence of "active" hydrogen atoms in the molecule can give dual function antirads which limit free radical reactions as well as acting as energy absorbers.

Many of these antirad materials are insoluble or sparingly soluble in lubricating fluids, and this imposes a restriction on their use in liquid products. In greases, however, no manufacturing or performance disadvantages have been observed in the formulation of three- or four-phase systems provided that phase dispersion was adequate.

To illustrate the value of such additives, the Bentone 34/alkyl phenyl silicone grease referred to in the previous section was selected on account of its relatively poor radiation resistance. A number of antirads of the two types were incorporated in the base grease during manufacture and the products tested by both static and dynamic irradiation techniques.

Static Irradiation Data

A number of polycyclic aromatics was separately added to the base grease to give three levels of antirad concentration. A grease was also compounded to include a free radical scavenger. These various products were irradiated in the Harwell gamma facility to dosages of 300, 500, 700, 1000, 1500 megarads and thereafter tested for consistency change, mechanical stability, and oxidation stability. A summary of the more pertinent findings is given in Table IV.

In general, the degree of protection afforded to the base grease varied directly with antirad concentration, but it was observed in some instances that high antirad concentrations could affect adversely the structural stability of the base grease. There was also a tendency for little further benefit to be derived in increasing the antirad concentration above a given level.

Antirads involving four-ring (condensed) structures were the most effective of those tested, with few significant changes in grease characteristics being observed up to the 1500-megarad level. Other materials were less effective according to the limited possibilities of resonance within their structures. In Fig 5 the per cent change in unworked penetration is plotted against the logarithm of the received dosage for a number of the antirads at equal concentrations. The improvements over the base grease without additives can be clearly seen.

Selected greases irradiated to the 1000-megarad level were rig tested on the IP rig under the conditions

TABLE IV

Antirad Evaluation—Static Irradiation Data

Grease	Antirad	Summary of effects of irradiation
Bentone 34/alkyl phenyl silicone	Nil	Unworked penetration—pronounced stiffening at 700 megarads Worked penetration—softened to 500 megarads, then stiffened Oxidation stability—reduced at 500 megarads
	3-ring (uncondensed) polymer	Unworked and worked penetrations—no significant change to 1000 megarads; protection afforded proportional to antirad concentration Mechanical stability—unaffected at 1000 megarads Oxidation stability—little changed at 1000 megarads
	10-ring (partially condensed)	Unworked and worked penetrations—softened appreciably at 500–700 megarads; excessively stiff at 1000 megarads Mechanical stability—constant until influenced by fluid polymerization
	3-ring (condensed)	Unworked and worked penetrations—no significant change to 1000 megarads; some stiffening in unworked penetration at 1500 megarads Mechanical stability—apparent improvement with increasing radiation dose Oxidation stability—some deterioration in the 700–1000 megarad range; severe by 1500 megarads
	4-ring (condensed)	Unworked and worked penetrations—no significant change to 1000 megarads Stiffening at 1500 megarads inversely proportional to antirad concentration Mechanical stability—apparent improvement with increasing radiation dose
	4-ring (condensed-dihydro) "B"	Unworked and worked penetrations—little change to 1000 megarads At 1500 megarads unworked penetration stiffened and worked penetration softened Mechanical stability—unaffected at 1000 megarads
	4-ring (condensed) "C"	Unworked and worked penetrations—no significant change to 1500 megarads Mechanical stability—unaffected to 1000 megarads. Some deterioration at 1500 megarads at high antirad concentrations Fluid separation, Drop point } Deterioration at high antirad concentrations

previously defined (Table V). With the four-ring (condensed) structures, performance was little different from that of the unirradiated base grease without additives. There was little to choose between the dihydro compound " B " and the corresponding aromatic " C." Where the irradiated greases were tested at several antirad concentrations there was a definite tendency for rig performance to suffer as the antirad concentration was increased. Once again, the order of performance supported the hypothesis that antirad effectiveness depends upon the resonance energy associated with its structure.

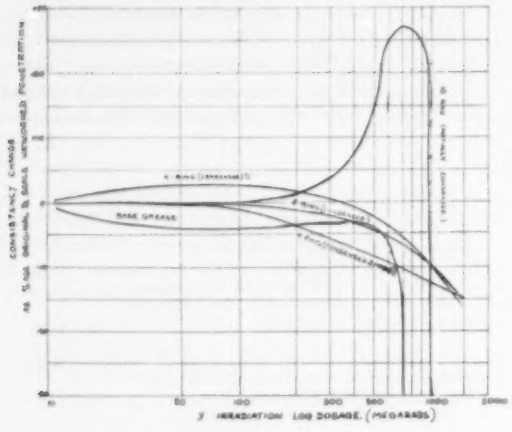

FIG 5

ANTIRAD EVALUATION. CONSISTENCY CHANGES *v.* IRRADIATION

Dynamic Irradiation Data

The results from three test " runs " on the SETRA rig are summarized in Table VI. The tests were stopped when one of the four bearings failed due to over-temperature running or excessive developed torque. The rig was then either stripped and examined or subjected to an additional period of static irradiation.

The effectiveness of antirads in protecting the base grease is well illustrated, with the order of performance similar to that observed in the static irradiation tests.

The first test run demonstrated that antirads of the " energy absorber " type can effectively increase the life of the lubricant. These results, taken together with those of the second run, defined the order of effectiveness as 4-ring (condensed) > 3-ring (condensed) > 3-ring (uncondensed polymer). In the final series it was shown that the combination of " energy absorber " and " free radical scavenger " antirads can give a further boost to performance.

It should be stressed that although the base grease used in these experiments was formulated from

TABLE V

Antirad Evaluation

Static Irradiation Followed by Dynamic Tests

(IP Rig—Air Atmosphere)

Grease	Antirad	Received dosage, megarads	Hours to failure	Temp, °C	Test ratings*				
					Softening or hardening	Leakage	Lubrication	Bearing wear	Cage wear
Bentone 34/alkyl phenyl silicone	Nil	Nil	500+	120	1	1	1	1	1
			500+	150	2	1	1+	1	1
			167	200	3	2	4	2	1
		100	500+	150	2	1	1	1	1
		500	212; 247	120	4	1	3	1	2
					4	1	3	1	1
	Free radical scavenger	500	500	120					
			+256	150	4	1	4	3	3
	3-ring (uncondensed polymer)	500	500	120					
			+256+	150	3	1	3	1	1
	3-ring (condensed)	1000	(*a*) 93	200	3	2	3	2	1
			(*b*) 47		4	2	3	3	1
	4-ring (condensed) " A "	1000	(*a*) 143	200	4	2	3	—	—
			(*b*) 99						
	4-ring (condensed-dihydro) " B "	1000	(*a*) 137	200	4	2	3	2	1
			(*b*) 112		4	2	3	2	1
			(*c*) 77		4	2	3	—	—
	4-ring (condensed) " C "	1000	(*a*) 140	200	4	3	3	2	1

(*a*) → (*c*) increasing antirad concentration.

* Rating system as IP 168/59T.

materials of poor radiation stability, some of the compounded products were capable of withstanding 1,000 megarads without appreciable change in structure or lubricating ability. The limits of performance when these antirad materials are used in conjunction with stable thickeners such as calcium complex soaps, selected pigments, etc., and stable fluids of the polyether family, have yet to be defined.

TABLE VI

Antirad Evaluation

Dynamic Irradiation Tests (SETRA rig)

Grease	Antirad	Received dosage, megarads		Hours	Temp, °C	Bearing and grease condition
		Dynamic	Static			
Bentone 34/alkyl phenyl silicone	Nil	65	Nil	390	150	Bearing—seized Grease—hard and black
	3-ring* (uncondensed) polymer	60	Nil			Bearing—free turning Grease—heterogeneous and dark
	4-ring (condensed) "A"	115	Nil			Bearing—free turning Grease—dark but otherwise unchanged
	4-ring (condensed-dihydro) "B")	120	Nil			Bearing—slightly rough Grease—unchanged
	3-ring* (uncondensed) polymer	120	650	1884	150	Bearing—seized Grease—dark, rubbery
	3-ring* (uncondensed) polymer	120	660			Bearing—seized Grease—dark, rubbery
	3-ring (condensed)	120	650			Bearing—very stiff Grease—dark, stiff but still plastic
	4-ring (condensed) "C"	120	660			Bearing—slightly stiff Grease—dark, slightly stiff
	3-ring* (uncondensed) polymer	1000	Nil	2700	100–110	Bearing—seized Grease—carbonized, stiff, rubbery, dry
	3-ring (uncondensed) polymer + Free radical scavenger	1000	Nil			Bearing—free turning Grease—dark, very slightly stiffened. Otherwise unchanged
	4-ring (condensed) "C"	1000	Nil			Bearing—free turning Grease—stiff and tacky
	4-ring (condensed) "C" + Free radical scavenger	1000	Nil			Bearing—free turning, dark, very slightly stiffened. Otherwise unchanged

* Different concentrations.

CONCLUSIONS

The response of a given grease to radiation is a complex phenomenon involving: (1) the composition of the grease; (2) the manner in which it is exposed to the radiation; and (3) the means by which its response is evaluated. Therefore it is unwise to predict the utility of a grease in any specific situation without having tested it in circumstances approaching those under which it is to be used.

Progress has been made in learning how to test and select specific grease compositions to meet specific needs, where radiation level, atmosphere, temperature, and the other important variables can be stated.

ACKNOWLEDGMENTS

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DISCUSSION

N. A. Scarlett (" Shell " Research Ltd): As most of us are aware, this year 1961 will see the opening of the first commercial nuclear power reactor in the U.K. This is of significant importance to the oil industry in that, for the first time, lubricants will be required to operate in a completely new environment, namely, that of high energy ionizing radiation. This, as we know, can be extremely damaging in its effect, giving rise in lubricants, for example, to increases in viscosity and eventual solidification, a most undesirable state. Therefore, for some years now the oil industry has been working to develop oils and greases which will perform satisfactorily under these novel conditions. Thus, any paper which adds to our knowledge of this fascinating subject is welcome.

The authors' results in the SETRA rig show that suitable antirads give a definite lift in performance when used in a grease system containing a fluid of relatively low radiation stability. Would the authors expect a similar improvement if antirads were used in a grease which contains naturally occurring aromatics in the base oil (which in themselves can be thought of as antirads) and is stable up to a dosage of about 2000/3000 megarads?

There are two points which arouse some doubt in my mind on the results presented in Table VI. In the first instance no base line has been obtained for the unirradiated grease, and secondly, only one test has been made on the grease without antirads. Can the low life obtained be due to a faulty bearing? This low life does not agree with the results obtained in the IP rig, which was run under more arduous conditions, namely, at the same temperature but in air at higher dmn values and greater radiation dosage. The life in the SETRA rig was also at variance with the expected performance predicted by the laboratory tests presented in Table III.

It would also be interesting to know at what concentration the antirads were used. The function of an antirad is such that one might expect fairly large concentrations would be necessary before a worthwhile effect is obtained. This, of course, is a drawback to their use, and in fact one interesting point of comparison might be made with the field of anti-oxidants, which, by virtue of their chain breaking properties, are extremely effective at very low concentrations.

The data presented in Table III would be more informative if the radiation stability of the base fluids was given. Furthermore, some indication is necessary to define quantitatively what stiffening and softening of the grease means. For example, does the worked penetration lie within the limits of 200–330, which are likely to be those adopted in future specifications?

Some of the results are at variance with our own experience as far as certain gelling agents are concerned. We found Estersil to be very stable. This difference might be due to our static radiation tests having been carried out at 80° C, whereas the authors' work was done at 25° C. This raises the problem as to whether the temperature of radiation is critical.

W. Crawford: We expect to derive appreciable benefit from the use of antirads in greases which already contain aromatic nuclei in the molecular configurations of the thickener and/or lubricating fluid. Where fluid polymerization is not a limiting factor, antirads can function by delaying the discontinuities in thickening power noted even with highly aromatic thickeners under static irradiation conditions. The energy absorbing capacities of some of the polynuclear antirads described are greatly in excess of those of aromatic materials that must also function as thermally stable, fluid lubricants.

With regard to antirad concentration, this can be limited to below 30 per cent by adverse effects on the grease structure. Whereas, in general, protection increases with antirad concentration, there would appear to be an optimum for any given " energy absorber " type of antirad above which little additional benefit is derived. With radical scavengers the additive is used up in performing its function, and thus the greater the concentration, the higher is the degree of protection afforded.

The inconsistencies in rig test durations between the IP rig and the SETRA rig have been noted and, in general, the results that we have obtained from SETRA have been somewhat lower than we expected from corresponding tests on the IP rig. I do not think that close correlation between such dissimilar apparati can be expected. Differences in bearing size and geometry, windage, atmosphere, and the developed torque necessary to cause rig stoppage are, no doubt, contributing features. With respect to atmosphere, better performance would normally be expected in a carbon dioxide environment as opposed to air. This supposition has not always been verified, and I think that the majority of us were disappointed in finding that carbon dioxide was not as inert an atmosphere as we had believed.

J. J. Frewing (Shell International Petroleum Co. Ltd): As the authors mention, for some applications on nuclear

power stations, such as the control rod mechanisms, it is essential to have a grease which will operate without any trouble for periods up to five years. For such a grease the volatility is a very important aspect and, in fact, the Atomic Energy Authority is putting volatility clauses in its specifications for greases for nuclear power plants.

Even if the base fluid has an extremely low vapour pressure, over a period of five years at temperatures around 150° C the grease might dry out. I wonder if the authors could comment on the relative volatilities of the three types of systems they use, *i.e.* the three base fluids, the bright stock, the silicone, and the phenyl ethyl ether.

My second point concerns oxidation stability, and in particular Table III. The authors state that they find stability at 500 megarads was impaired to the extent of 50 per cent of the original. Could they comment on how that was assessed, what type of test was employed, and what particular criterion was adopted in arriving at that?

W. Crawford: On the question of volatility there are two factors. First, with regard to reactor contamination perhaps this is a problem that has been overstressed. It would be an interesting exercise to calculate the total volume of volatile matter, assuming complete volatilization of all grease in reactor components, and relate this to the volume of gas coolant and its rate of loss compensation. The second factor is drying up of the lubricant, and in this respect we found the petroleum oil superior to the particular silicone fluid employed. Silicone fluids of this type normally contain small amounts of light ends. To remove these is, I understand, a relatively expensive process, and the less volatile residue would have inferior radiation stability. With the di- and poly-phenyl ethers there is such a range of these materials that it is impossible to generalize with respect to volatility, but this is one of the necessary considerations in selecting a particular ether for a given application.

In relation to UKAEA volatility requirement, a grease compounded from Bentone 34 and a petroleum bright stock as used in this work meets the Part I specification. A similar product employing methyl phenyl silicone fluid and the same additives fails by a narrow margin.

Oxidation stability has been defined throughout this work by means of static bearing oxidation tests and/or rig tests carried out on the Annapolis rig in a carbon dioxide atmosphere. Both methods have their limitations. In the particular instance referred to, the 50 per cent degeneration was assessed on the basis of rig life.

J. R. Ridley (General Electric Co. Ltd): I would like to endorse the remarks made by the authors concerning the use in reactor design, whenever possible, of established engineering practices. Centuries of experience have gone to show that it is highly desirable to use lubricants in bearings. But in the nuclear field this must be qualified, for reasons other than mechanical, by the phrase " where the circumstances allow." If lubrication is possible, corrosion problems are reduced and special materials become unnecessary, with consequent saving not only in cost but also in wear and tear on the personnel who have to find these materials and develop them. In addition, the protracted and difficult deliveries associated with " specials " are avoided.

The authors set themselves a target of developing a grease with a shear stable structure after irradiation to 2000–3000 megarads, and seem to be within sight of their goal. What are the prospects of meeting the temperature requirements of 250° C in the near future? Since, in the main, higher radiation and high temperatures go together, can the authors give any indication of possible time scales involved in achieving their objectives? And can they forecast from their present state of knowledge what is the ultimate that they may be able to achieve?

A difficulty in reactor operation is that these extremes of operating conditions are frequently met in equipment that becomes too hot radiation-wise for regular or, in fact, any maintenance.

The comments on the effects of radiation on penetration values are rather interesting. Have the authors ever found a grease, possessing similar penetration values before and after irradiation, which, after irradiation, could be useful or would compare with the original grease?

A further point is that on examining grease after service, in view of the apparent balancing effect of fluid polymerization and structure change, is an operator likely to have difficulty in deciding whether a complete replacement of the grease is necessary or not?

From the applications point of view, it is interesting to note that the authors found a 40 per cent reduction of applied gamma dose in certain locations within the SETRA rig, due to the shielding effect of the bearing housing, etc. It is highly probable that, in practice, dosages actually received by the bearings would be a good deal less than have been estimated, with consequent potentially longer working life of the grease, particularly in view of the fact that radiation levels have in the main been estimated on the high side.

Finally, a recent technical publication made mention of the shear breakdown of certain greases when stored in high and low humidity environments. In view of the low moisture content of the gas in reactor circuits, and the fact that bearings in certain circumstances remain static for considerable periods, do the authors think that any difficulties of this nature may arise with the type of lubricants they have investigated?

Dr D. B. Cox: The first question was when do we think we might get to the goals set in the paper regarding radiation and temperature? To be completely honest, I would say that we do not know; to go further than that, I would say that we have materials in mind and means of putting them together, which leaves us with getting the proper tests on these in the minimum length of time necessary. If we run these tests, and see that there are problems not anticipated, or that the greases do not work as well as we hope they will, the answer would still be " I don't know." If we are lucky, it could be not too far away.

The second question was just how far can materials available to-day be pushed? This is a little difficult to answer exactly, but I would say that, in organic materials, the limit is probably already pretty near for things that can be treated both as lubricants and still have the radiation resistance. When I say near, I am assuming that the limit approaches 5000 megarads. I do not know of anything which is also a lubricant that goes beyond that to-day. There are organic materials which are being used as moderators in power plants in the U.S.A., such as terphenyls, but the basis of success in their use is not so much the life of a charge, but the fact that make-up moderator can be added to the reactor as it runs along. Every day there is some moderator consumed by the radiation, as it were, which needs to be replaced. I suspect that even the terphenyls would not have a radiation life beyond about 5000 megarads.

With the thickeners, we are also near the same limit, I think. The limitation is inherent in the type of chemical bond in organic materials. Metals, ceramics,

and materials of crystalline bond composition will take a great deal more radiation than organics, but there are few thickeners in this class as yet. Silica and carbon black can be thickeners, but other problems arise in their use.

Mr Ridley asked whether we had a grease which was really essentially unchanged at some point of radiation; in other words, did it have the same consistency and so forth after it had been irradiated as it did before? We could show greases that had the same penetration but, as was pointed out in the paper, penetration is something that is not sufficiently revealing as a measure of consistency. One has to distinguish between the yield and the response at low shear and higher shear. I doubt if a grease would be exactly the same unless it had been to a relatively low level of radiation, but it is quite possible, on the other hand, to have a grease stay quite level on penetration up to some relatively high dosage.

There was also a question about how an operator of a plant could tell when the lubricant needed to be changed, or whether it were safe to leave it in for a further lubrication interval. I think that is very difficult. All we can do is to try to test under conditions as closely approximating the final use as possible, and then predict from that sort of test. It may be possible in future to devise tests which will reliably predict remaining grease life. One such test might be an examination of flow properties in a cone-plate viscometer. There are possibilities there, but I think it is necessary to rely on experience, from actual plant operation, before we can say certainly how much further a given lubricant can be used.

With regard to the question as to whether there is going to be any problem with static storage stability, of greases that are in a bearing and exposed to varying humidity, it does not seem likely that conditions encountered when the grease is static will be more severe than dynamic ones. I would not anticipate special problems on this point.

W. Crawford: I would add that most of the greases that will be used in these nuclear applications are non-soap in nature, and that storage stability problems are not normally so prevalent with greases of such composition as with some soap products.

Dr D. B. Cox: Concerning the radiation levels being lower than expected, we feel the same way as Mr Ridley on that. The estimates which have come out on these plants have been taken to give a safety factor and, in developing lubricants, our goal has always been to provide lubricants which will give you as great a safety factor as possible. We would very much like to provide the best possible lubricants, so that one would be certain that when the machines are started up they will work.

Dr A. L. Morris (Esso Research Ltd): Whilst agreeing with previous speakers regarding the merits of the paper, I do feel it would be more useful if we had been given further information. I note, for instance, that in no case are we told how the greases are made, or the percentage thickener used, and particularly the penetrations of the greases before and after test, and I think these would have real bearing on the results obtained. For example, one would expect that for a grease which thins on irradiation, the thicker the grease one puts in a bearing, within limits, the better the results which would be obtained at the end.

Like Mr Scarlett, our results on the behaviour of gelling agents under irradiation do not always agree with those given in the paper, and we agree that this may be the effect of temperature. His experiments were carried out at 80° C, and the authors have carried out theirs at 25° C; we have done them at both 25° and 100° C. The 100° C data were obtained using a linear accelerator, and those at 25° C using the Harwell facility. We found that the Harwell facility was somewhat less severe. Whether this was a question of temperature or due to the rate at which the energy was supplied, I am not quite sure. In one case 1000 megarads is absorbed in about four weeks, and in the other in a matter of a few hours, so this may explain some of the discrepancies that occur.

Another point that I would like to raise, which has not received enough stress in the meeting, is protection of the oil by a thickener. With all the non-soap thickeners we have found that the base oil in a grease suffers far less damage than the base oil irradiated alone.

Regarding the mechanism of the breakdown of greases by radiation, which Mr Crawford said that he did not wish to discuss in any detail, I think too much stress has been laid on the chemical aspect of the attack induced by the irradiation; in other words, the formation of free radicals and their subsequent reaction, etc., and too little on the question of the energy supplied to the system by means of the ionizing radiation. It is well known that the greases are thermodynamically unstable gels, and if they are provided with energy, *e.g.* by means of a grease worker, a rolling stability tester, or ionizing radiation, there is a tendency to break the structure down. It is quite significant that, in almost all cases quoted in the paper, the grease actually thins on irradiation, despite the fact that it is well known that the base oil itself is thickening up considerably. I suggest that what is happening here is that the ionizing irradiation is breaking down this gel structure, which, after all, is only formed from rather weak van der Waal's forces between the thickener molecules and the base fluid molecules, and that the more energy supplied, the more the structure breaks down.

We have some evidence which substantiates this theory from work with carbon black, which is a thickener quite unaffected by radiation. These greases also thin on irradiation, despite the fact that the base oil thickens up considerably. I think the only explanation which can satisfactorily explain these facts is that the gel structure has been broken down by the energy supplied to the system.

Finally, on the question of the effect of high temperature, I am glad to see that Mr Crawford did stress this at the beginning of his talk. I thought it was glossed over in the paper, but anyone who has worked on radiation resistant greases will be aware of the fact that, although radiation poses many problems, the high temperature requirements are currently more difficult to satisfy.

W. Crawford: As regards the preparation and composition of the individual greases described, all were made by conventional methods which are described in published work or patents. We endeavoured where possible to produce products in the NLGI No. 2 consistency range.

The percentage thickener was, in every instance, the minimum consistent with meeting the penetration requirement, and polar dispensing agents were used where applicable. With some thickeners—particularly dye pigments—approximately 20–25 per cent thickener was required to achieve a No. 1 consistency grease. The nature of the lubricating fluid had a marked effect on the amount of thickener required to achieve a given penetration.

Details of formulations, manufacture, and tests were omitted from the paper in consideration of their limited value and excessive volume.

Dr D. B. Cox: One of the points raised was in connexion with the possibility of rate effects in testing studies. Rate effect does concern anybody working in this field, and what it really comes down to is the choice between waiting a longer time to obtain something like a gamma radiation, or taking the quick way out by using an electron accelerator to get the energy in quickly. Aside from the real question of whether there are rate effects, and some evidence that there are, it is desirable, if one has the time, to do any testing under conditions as closely approximating to the use aimed at as possible.

I might also say, in reply to the question about the details of our work, that we would not set forth this paper as a recipe for anyone to bother with as a means of going about this sort of work. As with any research and development, it is easy to say how it should have been done after it is finished. Rather than lead someone along our primrose path, we felt it best to keep to the conclusions that we felt were most important.

The question about whether a grease is thermodynamically unstable or not is one which can lead into considerable argument. It is possible for a system not to be at equilibrium, yet have such slow kinetics that it does not matter. I think many greases are slow enough to change under shear, so that one need not worry whether they are thermodynamically unstable or not. Also, we have seen greases that thin out at one rate of shear and thicken at another, yet the grease is absorbing energy at both shear rates. Most greases, when sheared in a cone-plate viscometer, show thinning at increasing shear rates, followed by partial, or even complete, recovery of structure if the shear rate is reduced. Finally, we have seen greases that stiffen directly on radiation. To sum up this point, I would say that while radiation energy must alter a grease in some way, it is too simple to state that it must break down the gel structure just because it is energy.

If I may digress a little, I would like to explain the flow curves of Fig 1. On the first three of these graphs there is a line starting out from the origin which goes out sharply to the right, comes back, and then goes up again and so forth. If this data had been plotted in a more absolute form, rather than as a copy of the raw data, the graph would show the origin of each curve starting somewhere on the shear stress axis and then going up. What that first line coming up from the origin represents is an instrumental quirk, rather than a true picture of what is going on in the grease itself. It represents the winding up of a torque spring which is used as the sensing element in the cone-plate viscometer. The rest of the curve is quite accurate and indicative, and what it shows in these cases is that one gets some hysteresis in the programme of the flow curve, *i.e.* as one goes up the curve, the grease stiffens or breaks down to some extent, and as it comes down again it is at a slightly different viscosity because of time dependence and structure change. It will be noted, in the first two of these graphs, that the down curve comes in to the shear stress axis with a finite stress at the same time that shear rate has dropped to zero. This is merely an expression of the fact that this grease does have a yield value which is persistent after shear, and is an expression of the fact that the thickener particles want to hang together.

In the third flow curve (250 megarads), the ability to retain a yield is dropping off, and, finally, the last graph shows that the structure which contributes to the yield of the grease is pretty well gone and there is essentially a fluid.

One other minor point was the question of the temperature of irradiation, and disagreement in the results on "Estersil." The temperature might well be at least a partial explanation; another part might be the fact that it was perhaps a different "Estersil." This is not a satisfying explanation, but it is sometimes a little difficult to duplicate one's own results, let alone obtain agreement between laboratories.

The same is true with bearing testing. I recall a recent case in the U.S.A. where we were testing greases at 600° F in a high-speed ball bearing rig. Preliminary results from three laboratories showed that in one they got an average of about 40 hours, in another an average of about 70 hours, and in the third an average of 300 hours, all on the same grease. This goes to show that one should not really be too surprised by lack of agreement between laboratories on bearing test methods.

H. H. Heath (English Electric Co. Ltd): The authors have done their infra-red radiation work purely with gamma, I take it, and I wonder if they could tell us what the energy of that gamma is. Do they think that when greases are irradiated in a reactor where there are fast neutrons, thermal neutrons, and gamma, that the same sort of results will be obtained?

W. Crawford: We particularly chose gamma because we feel that in the majority of applications where the use of greases is feasible, gamma radiation will predominate. I am not in a position to quote the energy associated with the gamma radiation that we used, but the 50 per cent loss effect in the SETRA rig with a limited amount of interfering material suggests that the radiation was not of a high energy level. The gamma source was spent full elements from the DIDO reactor.

As to the equivalence of gamma irradiation and neutron bombardment, this will vary according to the material, but, in general, we have accepted the broad concept that, for hydrocarbons, different types of irradiation may be equated on an energy absorption basis. Thus there is a probability of error in translation from one type of irradiation to another.

Dr D. B. Cox: Between our two laboratories and countries we have subjected at least some of the greases in question to different types of irradiation. As Mr Crawford said, at Harwell the source is spent fuel rods, which means one obtains a spectrum of gammas coming from different isotopes with different characteristic energies. In the U.S.A. we have done some of the testing in gamma facilities using cobalt-60, which has two strong gammas, 1·1 and 1·3 Mev. We have also done a limited amount of testing in the Brookhaven pile. Any pile gives a broad spectrum of neutrons and gammas, which makes dosimetry more difficult. We have found that as good a way as any to check dosimetry is to assess the damage to the fluid part of the grease. This is not entirely safe because one does not know what sort of screening effect the thickeners had, but, if nothing better, one can obtain a rough idea of dose from how much one has polymerized and thickened the fluid. It is possible to extract it from the grease after irradiation and measure the viscosity, and if one has done enough samples, one can plot a curve of viscosity *v.* irradiation and use that as a dosimeter. In cases where that was done, we found reasonable agreement between radiation sources.

We have not done any work with electron accelerators. It was all done with gamma, spent fuel rods, or a pile.

Dr R. Irving ("Shell" Research Ltd): There are two points I should like to mention. First, the authors report work on the effects of radiation on the oxidation stability of greases, these tests being carried out after the

grease had been irradiated. There is a possibility, however, that in the future one might have to lubricate in the presence of air and irradiation—in other words, under conditions in which both oxidation and radiation reactions will take place simultaneously. Both reactions have common features in the sense that free radicals are produced in each case. In the case of oxidation testing after irradiation, however, all these free radicals will have been used up in some way; they will, for example, have reacted to form dimers and trimers, etc., and at the same time unsaturated materials will also be present. Therefore, I think that to test for oxidation stability after irradiation is to a certain extent unrealistic. A more realistic approach would be to irradiate and oxidize at the same time so as to get the effect of both reactions simultaneously.

The second point is that some years ago I looked at this question of the equivalence of different types of radiation and their effect on hydrocarbon oils. We found that irrespective of whether one used cobalt-60 gamma radiation, beta radiation, or mixed radiation (thermal and fast neutrons together with gamma radiation), then the results on hydrocarbon oils correlated very well indeed as long as one worked on the basis of equivalent energy absorption.

W. Crawford: As to the advisability of assessing oxidation stability after irradiation, in the present work we used the loss of oxidation stability as one of the criteria of radiation damage as opposed to attempting to correlate it with grease life in service.

As I stressed in the paper, it is not sufficient to rely on static irradiation followed by dynamic testing. The other condition, where both degenerating factors operate simultaneously, must be considered. It is suggested that the latter is the more severe, but there is also evidence to the contrary.

A complete assessment of the radiation resistance of a grease can be obtained only by studying its behaviour under static and dynamic conditions of irradiation and in the presence and absence of other damaging influences.

R. Tourret (Esso Research Ltd): I noticed in the paper a reference to Nilos seals in the SETRA rig. As the audience probably knows, these are little tin lids, in effect, which are put on each side of the bearing, and I think those amongst us who are concerned with nuclear power stations have put these seals on to prevent the grease falling out if it liquefies. Of course, we in the petroleum industry are busily trying to make sure that the grease does not liquefy. This belt-and-braces attitude is probably typical and even desirable at the present state of the knowledge in this field.

However, when it comes to test work on the lubricant development side, if there is any liquefaction, we want to see it. We do not want it to be bottled in, so what we have done on one of the types of rig that we are running is to drill a series of small holes all round the tin lid, so the application has the desirable attribute that it looks the same as the application in service, but, at the same time, if the grease liquefies, which is what we are trying to prevent, we shall see plenty of it.

On another type of rig we are running, we tackled the problem in a somewhat different way. We packed out the Nilos seal with a washer on the shaft, so that if we had the washer inboard of the Nilos seal, *i.e.* between the seal and the bearing, there is a gap through which any liquefied grease can run. This is a somewhat more elegant solution, and also gives us the possibility, if we desire, of reversing the order with the washer outboard of the Nilos seal. We are then fully duplicating the service application. I wonder if the authors have given any consideration to that aspect.

Finally, one complete quibble, and that is in Table III, column 4, 300 megarads. This is a very long column, which, as far as I can see, has not a single entry.

W. Crawford: With regard to Nilos seals, we found that if these were tightly "run in" to the bearing faces, such additional drag was created that the motor on the SETRA rig was insufficiently powered to turn the shaft. We thus had to adopt a procedure whereby the seals were very lightly "run in" and, under these conditions, they do not prevent leakage. To prevent inter-bearing contamination arising from leakage we provided spinner plates between the bearings.

R. F. Wenborne (Castrol Ltd): As the authors will know, the UKAEA Schedule II specification calls for a rig test at 200° C. We have, over the years, conducted a considerable amount of work on a wide range of greases, including synthetic soaps, silica, carbon black, and bentone gels. It is our experience that, in general, greases based on inorganic gelling agents and carbon black, suitably formulated to meet AEA requirements, have a temperature limitation below 200° C. They may give a satisfactory bearing rig performance at 150° C under AEA Schedule I conditions even after a fairly large dose. However, at 200° C such greases do not show up well even before irradiation. This is not the case with certain synthetic soaps, and I would like to know the authors' experience of this, in view of the apparent favour shown by the authors and other speakers towards inorganic or carbon black gels for reactor lubrication.

The other point is that some years ago we carried out experiments involving the beta irradiation of various greases in the Wantage linear accelerator, covering a range of doses at different dose rates. Since that time we have used the Harwell underwater facility for gamma irradiating the same greases to the same doses. We found that the penetration figures, which are admittedly not a very reliable guide for assessing radiation stability, gave anomalous results—apparently a better performance the higher the beta dose-rate—but when evaluated in a rig the samples irradiated at the higher dose rates gave a very much poorer performance. The same greases irradiated in the spent fuel source have given much better bearing rig results than were obtained with nominally equivalent beta doses.

We concluded that radiation damage, as assessed by rig performance, is not necessarily independent of the type or rate of irradiation. However, other speakers' experience seems to indicate that damage is a function of energy absorption and is not influenced by the type of radiation.

W. Crawford: With regard to the temperature limitations of these various thickeners, there are two factors to be considered, namely, the maximum operating temperature, and comparative grease life at a given high temperature.

Most of the thickeners described are capable of limited operation at 200° C, particularly in a carbon dioxide atmosphere. However, for a life of 750 hours or greater at temperatures of 200° C and above, I think the most promising class are the inorganic pigments. One has been mentioned in the paper, but we have examined others which have given greases that withstood 315° C for several hundred hours when rig tested in an oxidizing atmosphere.

J. R. Ridley: The authors have covered the case of greases in a CO_2 atmosphere. Can they give any indication of whether any other gas, *i.e.* nitrogen, helium,

or other possible reactor coolant gas, is likely to have a different effect on the greases when they are irradiated? Or, put another way, will the irradiation effect on the grease be different in those types of atmosphere?

Dr D. B. Cox: There is one reactor at present being considered in the U.S.A. which is to be gas-cooled by helium, and there is consideration of that in the U.K. also, I think. I would anticipate that helium would be about as nice an atmosphere as one could possibly provide. I cannot say that we have tested anything directly in helium yet, but I will be surprised if it turns out to have any specific adverse effect of its own.

J. J. Frewing: There is some work published in the literature to the effect that a helium atmosphere or an inert atmosphere can introduce problems of its own in lubrication, because lubricated surfaces do depend to some extent on the oxide film, particularly under boundary conditions. If there is a completely inert atmosphere when one has worn off the oxide film it cannot be repaired, and there is some evidence that excessive wear can occur in certain cases in those conditions.

Dr D. B. Cox: It sounds possible, particularly if we are concerned with a completely dry atmosphere. Practical experience does show, however, that, with graphite moderated piles, reactor mechanisms operate in anything but a water-free atmosphere. Of course, what we are looking for is a grease to keep those oxide layers from wearing off.

Dr J. Mason (Chemical Inspectorate, War Office): I should like to ask about one or two standard tests which are used in assessing oxidation stability and which one sees in almost every modern grease specification, *e.g.* the Norma Hoffmann bomb test. Has this test been tried on irradiated greases, and what have the results been? Secondly, have irradiated greases shown any different corrosivity to metals? Thirdly, can one trace any changes in total acidity?

W. Crawford: The Norma Hoffmann bomb test has been used mainly to correlate with shelf life. We have never found it to have any significant contribution to make in the assessment of grease life under dynamic conditions. Even with regard to shelf life, its value is limited mainly to the older lime and soda base greases. Its application to greases subjected to ionizing radiation is perhaps more justifiable, since it may be used as a measure of olefin formation.

In assessing oxidation stability we have resorted to a simpler method, the static bearing oxidation test, which we believe tells us more in terms of grease life at high temperatures, structural changes in the grease, and fluid separation tendencies.

With regard to the formation of acidic material under the combined stresses of radiation and an oxidizing atmosphere, we have observed few instances of staining and none of badly corroded bearings.

Dr D. B. Cox: I might add that in the early stages of the work in the U.S.A., we irradiated three "conventional" mineral oil greases statically and measured Norma Hoffmann (ASTM) bomb oxidation stability. At 100 megarads none of them was substantially different from the unirradiated grease. We also determined the reaction of the greases which ordinarily contain an excess of alkali. We found that there was a reduction in the excess of alkali in those greases at those levels, but they had not gone over to the acid side. Finally, we have never seen any direct evidence of corrosion from greases, whatever their composition, either in static or dynamic irradiation.

Grease thickener	210° F, bomb oxidation, psi drop in 100 hours	
	Control	Irradiated
"Bentone 34"	17	20
Lithium soap	1	3
Calcium complex	3	3

The meeting then concluded with a unanimous vote of thanks to the authors.

IP ENGINE TESTS FOR RATING FUELS

It has been found necessary to make the following amendments in the engine test methods for rating fuels as published in the second edition of Part II of "IP Standards" (October 1960):

Pages 3 and 24

Replace the data in Section 6 (*b*) with:

26° at 0·625 in micrometer setting (basic setting)
25° at 0·573 „ „
24° at 0·521 „ „
23° at 0·469 „ „
22° at 0·417 „ „
21° at 0·365 „ „
20° at 0·313 „ „
19° at 0·261 „ „
18° at 0·208 „ „
17° at 0·156 „ „
16° at 0·104 „ „
15° at 0·052 „ „
14° at 0·000 „ „

Pages 30 and 55, Section 10 (*b*), line 5

Change ±0·3 ON *to* ±0·4 ON.

Page 115, Section 16

Change 4·2 Imp quarts *to* 3·0 Imp quarts
„ 3·6 „ „ *to* 2·5 „ „
„ 3·0 „ „ *to* 2·0 „ „

An amendment sheet is available and copies can be obtained from the offices of the Institute.

H H

THE EFFECT OF TEMPERATURE ON THE EFFICIENCY, RESOLUTION, AND ANALYSIS TIME OF CAPILLARY COLUMNS *

By R. P. W. SCOTT †

SUMMARY

The effect of temperature on column efficiency, resolution, and analysis time is considered theoretically. It is shown that the efficiency of a column for a specific substance will increase with temperature if operated at, or above, the optimum practical gas velocity. An optimum temperature is predicted that will give the maximum resolution for a given pair of substances on a given column.

It is also shown that for a column of a given diameter an optimum temperature and an optimum film thickness of stationary phase is required to produce the minimum analysis time. Experimental results for the separation of *n*-heptane/*iso*-octane and *n*-heptane/methyl*cyclo*hexane mixtures support the theory qualitatively. Values for efficiency, resolution, and analysis time obtained experimentally do not, however, agree well with theoretical values. Reasons for this disagreement are considered. If, for the separation of a given pair of substances, a capillary column is operated at a temperature other than the optimum, the analysis time may be inordinately long.

Symbols

$a = \frac{v_g}{v_l} = \frac{r}{2df}$	Ratio of volume of gas to volume of liquid phase in a theoretical plate
B	Longitudinal diffusion factor
C_g	Factor for resistance to mass transfer in the gas phase
C_l	Factor for resistance to mass transfer in the stationary phase
D_g	Coefficient of gaseous diffusion
D_l	Coefficient of liquid diffusion
df	Average film thickness
HETP	Height equivalent to a theoretical plate
K	Partition coefficient
$\bar{K} = \frac{K_1 + K_2}{2}$	
l	Column length
n	Number of theoretical plates
OPGV	Optimum practical gas velocity
r	Average column radius
t	Analysis time
u	Average linear gas velocity
v_g	Volume of gas per theoretical plate
v	Volume of stationary phase per theoretical plate

INTRODUCTION

THE effects of film thickness and of the volume of gas to volume of liquid ratio $(a) = v_g/v_l$ in a column, run at a given temperature, on the resolution‡ obtained and the analysis time§ have already been described.[1] A method for calculating the optimum film thickness to give the minimum analysis time, from the physical properties of solute and solvent, was also considered.

The resolution of two solutes, and their respective peak efficiencies, are not only a function of the a-value for the column, but are also dependent on a number of factors that vary with temperature. Similarly, the analysis time is also affected by the temperature. This paper describes the effect of temperature on efficiency, resolution, and analysis time obtained from a capillary column. It shows that, for a specific pair of substances separated on a given column of a particular a-value, an optimum temperature exists which affords maximum resolution. Both an optimum film thickness and an optimum temperature are predicted which would separate two given solutes on a given stationary phase in the minimum time. The practical results obtained for the separation of *n*-heptane/*iso*-octane and *n*-heptane/methyl*cyclo*hexane mixtures on two nylon capillary columns of different a-values using dinonyl phthalate as the stationary phase and argon as the carrier gas are given to support this theory.

THEORY

Effect of Temperature on Column Efficiency

The Golay equation[2] gives the following relationship for the HETP of a capillary column:

$$H = \frac{2D_g}{u} + \left[\frac{a^2 + 6aK + 11K^2}{24(a + K)^2} \cdot \frac{r^2}{D_g} + \frac{K}{6a(a + K)^2} \cdot \frac{r^2}{D_l}\right] u$$

It should be noted that the interfacial resistance to mass transfer, suggested by Khan,[3] is not included. The conditions under which this factor is experimentally significant have not yet been established and, as its inclusion might complicate the treatment unnecessarily, its effect is not taken into account.

If the column is run at or above the OPGV,[1] then the factor $\frac{2D_g}{u}$ will be negligible, hence:

$$H = \left[\frac{a^2 + 6aK + 11K^2}{24(a + K)^2} \cdot \frac{r^2}{D_g} + \frac{K}{6a(a + K)^2} \cdot \frac{r^2}{D_l}\right] u$$

* MS received 2 March 1961.

† Benzole Producers Ltd.

‡ The term resolution refers to the separation of a given pair of substances 1 and 2. The resolving power of a column is a function of the number of theoretical plates and the relative volatility $\left(\alpha_{1,2} = \frac{K_2}{K_1}\right)$. The higher the relative volatility, the less the number of theoretical plates required to achieve the separation. For difficult separations when relative volatility is close to unity, a column with a large number of theoretical plates is needed.

§ The analysis time refers to the time required to separate the peak maxima by a distance of four standard deviations.

where K, D_g, and D_l are all functions of temperature. The values of D_g at different temperatures can be calculated from the Gilliland equation,[4] those of D_l can be obtained from the Arnold equation,[5] using experimental data for the viscosity of the stationary phase, and K can also be determined experimentally. The values of K, for n-heptane, used in this paper were calculated from the data published for *cyclo*hexane by Adlard, Khan, and Whitham[6] and experimentally-determined retention ratios of *cyclo*hexane to n-heptane.

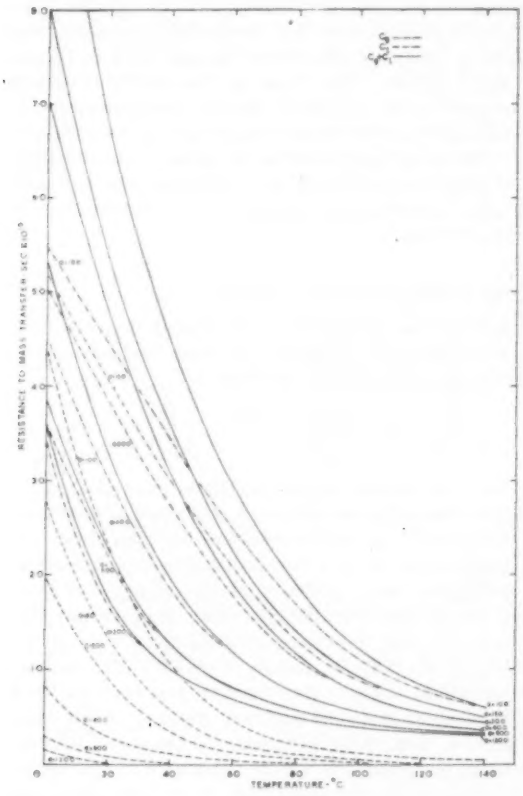

FIG 1

VARIATION OF MASS TRANSFER FACTORS FOR n-HEPTANE AGAINST TEMPERATURE FOR COLUMNS OF DIFFERENT (a) VALUES

Numerical values for the coefficient of resistance to mass transfer in the gas phase (C_g) and that for the stationary phase (C_l) were calculated for the n-heptane–dinonyl phthalate system, using argon as the carrier gas. These values were calculated for columns of fixed diameter (0·020 inch) but with different a-values, and the results obtained were plotted against column temperature as shown in Fig 1. The temperature range considered was from 0° to 140° C. In practice it is impossible to use dinonyl phthalate above 110° C owing to its high vapour pressure at this temperature. However, extension of the operating temperature range to 140° C allows the examination of the effect of change in temperature on the HETP over a wider range. It can be seen that C_l decreases rapidly with increasing temperature and becomes a negligible contribution to the total resistance to mass transfer term at about 60° C. The actual value of this factor at any given temperature decreases as the a-value of the column increases. The C_g value also falls as the temperature increases, but not to the same extent as the C_l term. Hence, the combined value of C_g plus C_l falls with rising temperature for columns of all a-values. This results in the column efficiency for a specific substance, increasing with the operating temperature for any given column. This effect has been suggested by Desty *et al.*[7] With a column of low a-value, the change in efficiency with temperature will be greater than for a corresponding column of high a-value. However, at any given temperature the column having the higher a-value will give the higher efficiency.

Effect of Temperature on Column Resolution

The resolution between two substances depends on the ratio of the distance between the peak maxima to the peak width at the base of either peak. Generally, it may be stated that, if the distance between the peak maxima equals the base width of one of the peaks, for practical purposes the substances are resolved. However, although the efficiency increases, and thus the peak width decreases, with increasing column temperature, the peaks also move closer together because their partition coefficients and their difference (ΔK) is also reduced. Thus it is not immediately obvious whether the resolution obtained from a given column will be greater or less at a higher temperature.

From the theory of the elution curve,[7] the ratio, Z, of the distance between two peak maxima to the peak width at the base may be expressed as:

$$Z = \frac{n\Delta K v_l}{4\sqrt{n}(v_g + \bar{K}v_l)}$$

where $\bar{K}$ is the mean partition coefficient of the substances concerned, ΔK is the difference between their partition coefficient, and n is considered the same for both components.

Thus, replacing $\frac{v_g}{v_l}$ by a and simplifying,

$$Z = \frac{\sqrt{n}\Delta K}{4(a + \bar{K})}$$

Thus, as $n = \frac{1}{H}$, substituting from the modified Golay equation:

$$Z = \left(\frac{1}{16u}\right)^{\frac{1}{4}} \cdot \frac{\Delta K}{r}\left[\frac{a^2 + 6a\bar{K} + 11\bar{K}^2}{24D_g} + \frac{\bar{K}}{6aD_l}\right]^{-\frac{1}{4}} \quad (1)$$

and, for a column of given length, operated at a fixed gas velocity,

$$\left(\frac{16u}{l}\right)^{\frac{1}{2}} Z =$$

$$Z' = \frac{\Delta K}{r}\left[\frac{a^2 + 6a\bar{K} + 11\bar{K}^2}{24D_g} + \frac{\bar{K}}{6aD_l}\right]^{-\frac{1}{2}} \qquad (2)$$

this assumes that D_g and D_l will have the same respective values for both solutes.

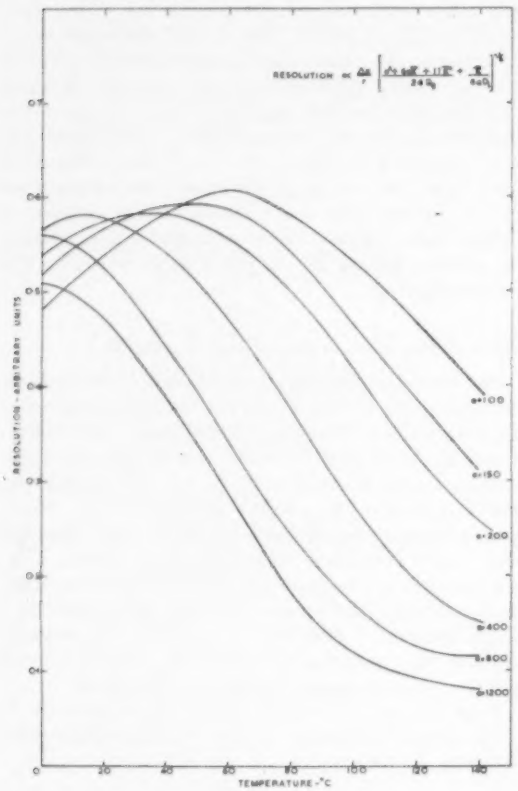

FIG 2

GRAPH OF RESOLUTION/TEMPERATURE FOR COLUMNS OF DIFFERENT (a) VALUES

The numerical value of the denominator in equation (2) was calculated for various operating temperatures in the manner described previously. For the separation of the two substances considered, ΔK was taken as equal to $0{\cdot}05K$ at all temperatures (*i.e.* the retention ratio of the two solutes was 1·05). This assumption implies that plots of log K against $\frac{1}{T}$ for the two substances would be parallel. This is approximately true for the majority of substances of similar type. Some exceptions to this generalization have been published, but they are comparatively few. The separation of substances of different types is not normally achieved by a change of physical operating conditions, but by a change in the nature of the stationary phase employed.[8]

Fig 2 shows a plot of Z' given in equation (2) against operating temperature. It can be seen that, for a column of a particular a-value, there is an optimum column temperature that will give the maximum resolution for the particular pair of solutes. An optimum temperature for maximum resolution was noted by Desty and Harbourn[9] in their work on Tide as a liquid phase. The value of the resolving power increases as the a-value of the column decreases. It should also be noted that columns having low a-values, *i.e.* with thick films of stationary phase, require higher operating temperatures, for optimum resolution of the two substances concerned, than columns having high a-values.

Effect of Temperature on Analysis Time

An equation giving the analysis time required for a given separation in terms of column and solute properties has already been published:[1]

$$t = \frac{2r^2}{3(\Delta K)^2}\left[\frac{a^2 + 6\bar{K}a + 11\bar{K}^2}{D_g} + \frac{4\bar{K}}{aD_l}\right]\frac{(a + \bar{K})}{a} \qquad (3)$$

An examination of this equation showed that, at a given operating temperature, there was an optimum value of a that gave the minimum analysis time. As a column can have a maximum resolving power at a particular temperature, it would appear that there will also be an optimum operating temperature that would give the minimum analysis time. Using the values of K, ΔK, D_g, and D_l obtained in the manner described in the previous section, the analysis time, t, for a given series of capillary columns of the same diameter, but with different a-values at different column temperatures can be calculated. The values of t obtained for the separation of the two substances having $\Delta K = 0{\cdot}05K$ on columns having a diameter of 0·02 inch are shown plotted against temperature in Fig 3. It can be seen that an optimum temperature giving the minimum analysis time does indeed exist, and that operating the column at a temperature other than the optimum may seriously increase this time. It can also be seen that the lower the value of a for the column, the higher the optimum operating temperature giving the minimum analysis time. The concept of an optimum temperature for minimum analysis time does not agree with the conditions suggested by Purnell and Quinn,[10] who claim that K should be made as large as possible while operating at as low a temperature as possible. However, as is subsequently stated by the authors, their predictions were for conventional-type columns where an even film of liquid phase may not necessarily be realized. The values of the minimum analysis times at the

optimum temperatures for the columns concerned decrease correspondingly with decrease in their a-value.

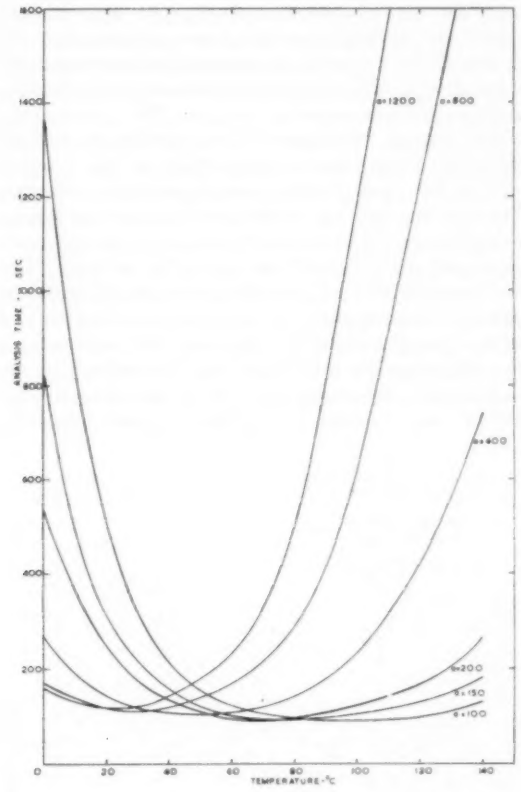

FIG 3

VARIATION OF ANALYSIS TIME WITH TEMPERATURE FOR COLUMNS OF DIFFERENT (a) VALUES

Effect of Temperature on the Optimum a-*Value of the Column*

The optimum a-value of a column, that will allow separation of a given pair of solutes at a fixed temperature in a minimum time, can be calculated from the following equation:[1]

$$1 + \left[\frac{a}{2K} + \frac{11}{8} Ka \frac{D_l}{D_g}\right] - \frac{7}{8}\frac{D_l}{D_g}\frac{a^3}{K} - \frac{1}{4}\frac{D_l}{D_g}\frac{a^4}{K^2} = 0 \quad (4)$$

As K, D_g, and D_l all change with temperature, so also will the optimum value of a. Using the same calculated values of K, D_g, and D_l for n-heptane, optimum values of a were determined from equation (4) for a 0·020-inch diameter capillary column at different operating temperatures. Graphs of both a and $\left(df \text{ calculated from the equation } a = \frac{r}{2df}\right)$ against temperature are shown in Fig 4. It can be seen that the optimum a-value of a capillary column separating the solutes concerned changes by a factor of 10 between operating temperatures of 20° and 100° C.

The optimum a-value for different temperatures was substituted in equation (3) with the corresponding values of $\overline{K}$, ΔK, D_g, and D_l. In this manner the minimum analysis time for each operating temperature was calculated using the respective optimum a-values. These minimum values for the analysis time plotted against temperature are shown in Fig 5. It is seen that there is again an optimum value for the minimum analysis time corresponding to both the optimum a-value and the optimum operating temperature. For a capillary column of the given diameter, this is the absolute minimum analysis time for

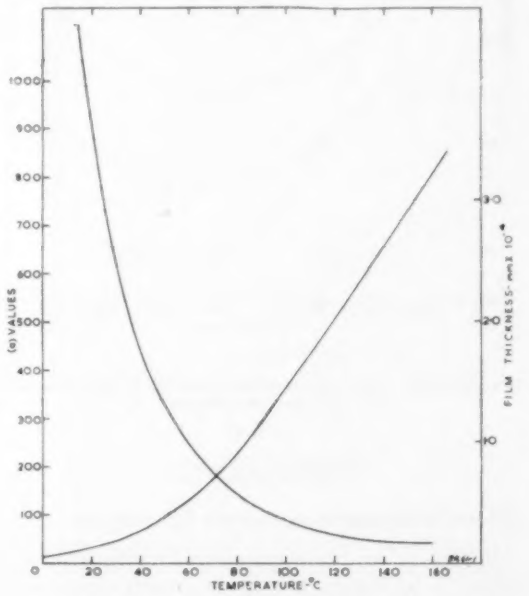

FIG 4

VARIATION OF OPTIMUM (a) VALUE WITH OPERATING TEMPERATURE

COLUMN: 0·02 IN. DIAMETER
STATIONARY PHASE: DINONYL PHTHALATE

separating the two substances concerned on dinonyl phthalate using argon as the carrier gas. It is unfortunate that this absolute minimum occurs, for a 0·020-inch diameter column, at a film thickness that is unstable on the smooth bore of the nylon capillary columns at present in use. However, from equation (4) it is seen that r does not appear explicitly, thus a is not dependent on a particular value of the radius, r. By reducing r, df may also be reduced to maintain the same a-value and the film could be rendered stable. Reduction of r also has the advantage of reducing the numerical value of the minimum analysis time for the column by a factor proportional to r^2. It is well

known that this process of rendering the film stable and reducing the analysis time has practical limits dependent on the sensitivity of the detector.

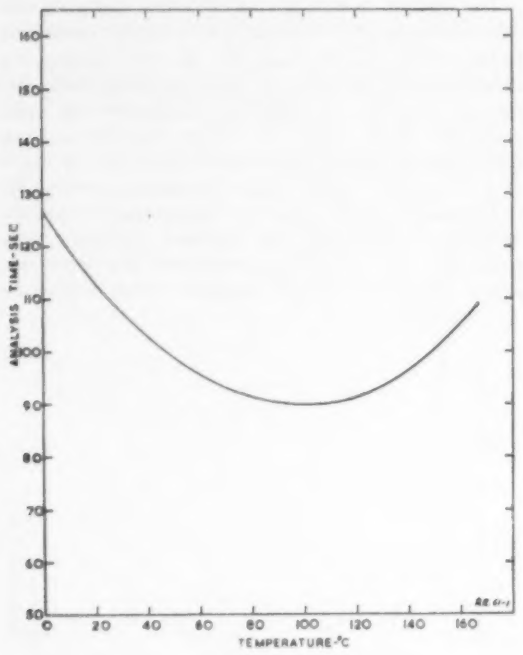

FIG 5

VARIATION OF MINIMUM ANALYSIS TIME WITH TEMPERATURE FOR COLUMNS OF OPTIMUM (a)

EXPERIMENTAL

Effect of Temperature on Column Efficiency

In order to compare experimental results with those predicted by theory, two nylon capillary columns A and B were employed, each 100 ft long. The diameters of short lengths taken from both ends of each column were determined by weighing known lengths filled with mercury. The diameters of the ends of column A were found to be 0·020 inch and 0·021 inch, giving a mean value of 0·0205 inch. The corresponding diameters for column B were 0·019 inch and 0·020 inch, giving a mean value of 0·0195 inch.

The columns were coated in the normal manner[1] using a 10 per cent solution of dinonyl phthalate in ether for column A, and a 20 per cent solution of dinonyl phthalate in ether for column B. The a-value of each column was determined by chromatographing substances of known partition coefficient and comparing the distance between the injection point and air peak for each column, with the distance between the air peak and the peak maximum for each of the substances used. Column A was found to have an a-value of 820 and column B an a-value of 430. These a-values correspond to film thicknesses of 0·16 μ and 0·29 μ for columns A and B respectively.

The columns, provided with the usual by-pass injection system, were situated in a suitable container that could be thermostatted at temperatures between 0° and 70° C. A micro-argon detector was employed together with a high input-resistance amplifier feeding a potentiometric recorder.

To examine the effect of temperature on column efficiency a fixed gas velocity of 40 cm/sec was employed for each determination on both columns. This gas velocity was maintained constant to within ±1 per cent. It was ascertained that the optimum practical gas velocity[1] was about 25 cm/sec. Thus at 40 cm/sec, the only significant factors affecting the column efficiency were the resistance to mass transfer in the gas and stationary phases. On each column the efficiency for n-heptane was determined at approximately 10° C intervals. From the efficiency, the HETP was calculated and the (C_g and C_l) terms

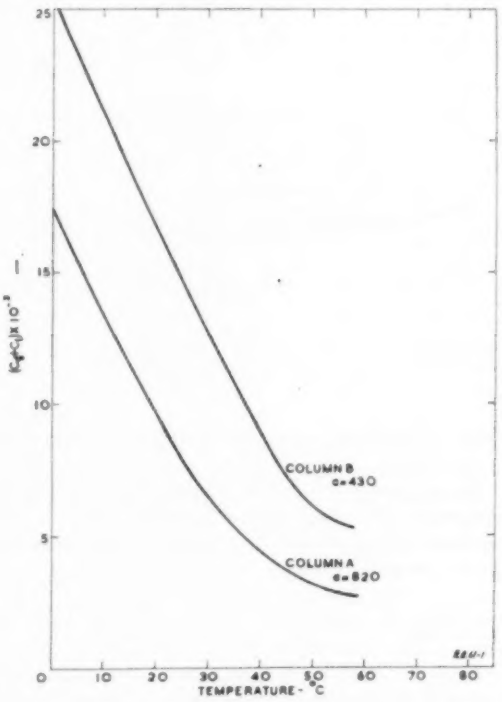

FIG 6

GRAPH OF $(C_g + C_l)$/TEMPERATURE

were determined from a knowledge of the HETP and the linear gas velocity. The results obtained are shown in Fig 6.

Effect of Temperature on Column Resolution

To examine the effect of temperature on column resolution, two pairs of substances were chosen which had retention ratios of about 1·2. As the retention ratios are not temperature-independent, the two pairs of substances were chosen such that the retention ratio of one pair increased slightly with temperature, while that of the other pair decreased slightly with temperature. The substances chosen were *n*-heptane and *iso*-octane with a retention ratio changing from 1·13 to 1·25 and methyl*cyclo*hexane and *n*-heptane with a retention ratio changing from 1·37 to 1·23 from 0° to 70° C respectively.

At approximately 10° C intervals the separation of each pair of substances on each column was examined at a linear gas velocity of 40 cm/sec. The separation was taken as the ratio of the distance between the peak maxima to the peak width of *n*-heptane. The results obtained for the separation of the two pairs of substances on the two columns plotted against temperature, are shown in Fig 7.

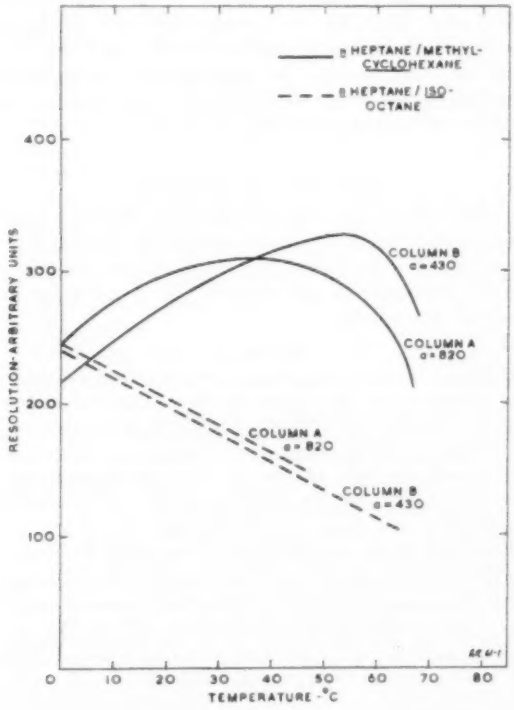

FIG 7

RESOLUTION/TEMPERATURE

Effect of Change of Temperature on Analysis Time

Using the same pairs of substances on the two columns, the time required to obtain the separation at various temperatures was determined. The relative proportions of the two substances in each mixture were adjusted to give the same peak height for each component on each run and the separation used was

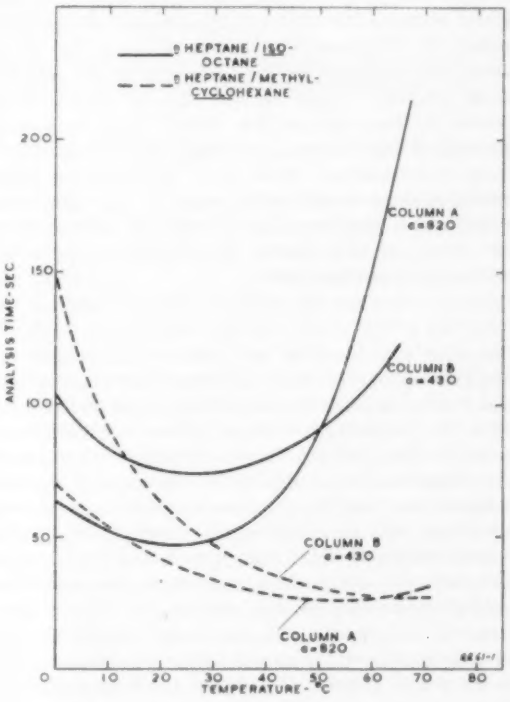

FIG 8

ANALYSIS TIME/TEMPERATURE

that which occurred when the minimum between the peaks was at one quarter of the height of either peak. The gas flow-rate was adjusted at each temperature to give this same separation between the two substances concerned and the time required for separation was determined.

The time required for the same separation of each pair of substances on both columns is shown plotted against temperature in Fig 8.

DISCUSSION

Curves showing the effect of temperature on the column efficiency, determined by experiment for the two columns, are shown in Fig 6. The shapes of these curves are the same as those obtained theoretically, as is evident from Fig 1. There is, however, a considerable difference between the experimental and theoretical values.

With column *A* having a thinner liquid film, the value of $(C_g + C_l)$ is lower than that obtained from

column B; this is in agreement with theory. However, the experimental values of $(C_g + C_l)$ are nearly five times the theoretical values. The excessive $(C_g + C_l)$ values are probably due in part to the high operating pressures required to obtain linear gas velocities above 30 cm/sec. Inlet pressures of 15 psig would increase the C_g term by a factor of approximately 2. In practice, pressures of about this value were used to obtain the necessary linear gas velocity of 40 cm/sec. If an uneven film of liquid phase existed in the column this would cause a serious increase in the C_l term. Another factor that could cause experimental results to be higher than those predicted theoretically is the neglect of any interfacial resistance to mass transfer.[3] However, judging from the shape of the curves, the results support the theoretical equations well.

Curves showing the effect of temperature on the resolving power of the columns are shown in Fig 7, and agree with the theoretical curves shown in Fig 2. The greatest resolution for the separation of *n*-heptane and methyl*cyclo*hexane was obtained on the column with the thicker film of liquid phase operated at an elevated temperature. Since the retention ratio of the *n*-heptane/*iso*-octane system becomes greater at reduced temperatures, the temperature for maximum resolution will be considerably lower. The experimental results for this mixture, shown in Fig 7, do not illustrate the optimum temperature for maximum resolution because it lies outside the temperature range investigated. The optimum temperature for the separation of the *n*-heptane/*iso*-mixture appears to occur well below 0° C. Again, the form and shape of the curves support the theoretical predictions.

Results obtained by experiment for the effect of temperature on analysis time are shown in Fig 8. Although the curves are of the predicted shape, they give a different impression of the effect of the a-value on the performance of the column. For the separation of methyl*cyclo*hexane and *n*-heptane, it may be seen that the fastest analysis would be obtained with a column having the lower a-value, at a temperature of 70° C. However, for the separation of *iso*-octane and *n*-heptane, where the *n*-heptane to *iso*-octane retention ratio increases with fall in temperature, the optimum temperature for the minimum analysis time is lower, at 25° C. The form of the curves obtained for the *iso*-octane/*n*-heptane separation agrees with that predicted by theory, but the minimum analysis time is obtained from the column with the thinner film and the highest a-value at a lower temperature.

It is worth noting that the values for the minimum analysis time obtained from the two columns differ by a factor of about 1·5. However, if the optimum temperature to give the minimum analysis time is not employed, the analysis time may be increased by a factor of 5 or more.

CONCLUSIONS

It may be theoretically deduced that any given column would have an optimum operating temperature to give the maximum resolution between any two given substances. If the retention ratio of the pair of substances concerned remains constant or increases with operating temperature, the best resolution will be obtained on a column with a thick film of stationary phase and low a-value, at a comparatively high temperature.

If the retention ratio of the two substances to be separated decreases with increase in temperature, then the best resolution would be obtained on columns with thinner films and higher a-values operated at lower temperatures.

It can be predicted theoretically that the minimum time of analysis (that can be obtained for a given pair of substances) requires a column that has an optimum film thickness and is operated at an optimum temperature. Experimental results support this view. Both the effect of the a-value and the operating temperature on the resolution and the analysis time can be considerable. If columns are operated at conditions far from the optimum, very serious increases in analysis time may result.

ACKNOWLEDGMENTS

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IDENTIFICATION OF CRUDE OILS BY PAPER CHROMATOGRAPHY *

By S. N. BHATTACHARYA †

SUMMARY

A paper chromatographic method with ethyl acetate as the developing solvent is described which permits detection of traces of crude oils in samples such as well cuttings, cores, drilling muds, oil emulsion muds, and surface samples, etc.

INTRODUCTION

STUDY of surface oil seeps and outcrops for bituminous materials, as well as detection of crude oils in samples such as well cuttings, cores, and drilling muds, are important in oil exploration.[1, 8, 9]

A number of methods such as: (1) micro-distillation;[2, 11] (2) fractional analysis;[7, 8] (3) studies of a few basic characteristics, such as per cent solubility in petroleum ether, elemental analysis, etc.;[12] (4) fluorescence studies with (*a*) drop,[8] (*b*) capillary,[3] (*c*) column chromatographic,[13] (*d*) paper-partition chromatographic [4, 5, 14] techniques, etc., have been reported in literature for identification and characterization of crude oils and bitumens.

Choice of a particular method for specific identification depends largely on the nature and amount of the sample as well as on the rapidity of the analysis required.

Of the methods available, micro-distillation [2] (which requires at least 0·8–1 ml as a sample) is the most specific for identification of crude oils, since, unlike distillate fractions (namely, diesel oil, kerosine, lubricating oil, etc.) crude oils will give cuts of all boiling ranges.

Fractional analysis, coupled with studies of the basic characteristics, under favourable conditions, leads to specific identification of bitumen samples containing practically no distillable fraction.

When the sample size is too small to run a micro-distillation and to investigate through fractional analysis, etc., fluorescence study is the only technique so far known for identifying crude oils. The three main constituents, asphaltenes, resins, and oily components of a crude oil, show different colours of fluorescence when irradiated with ultra-violet light. Asphaltenes present themselves as dark spots which become deep brown when wetted with solvent such as chloroform. Resins give yellow, orange, and brown colours, depending probably upon the increasing molecular weight and the complexity of the units composing those substances, while blue colours are exhibited by oily components. Almost all the commercial distillates of crude oils show blue fluorescence, although heavy distillates, on prolonged use in the machine may, however, show blue and light yellow fluorescence.

Crude oils, commercial distillates, solvent extracts of common drilling mud additives such as cutch (quebracho), lignites, humus materials, etc., all show blue to bluish yellow fluorescence in solutions of chloroform. Thus fluorescence studies in solutions are less specific.[3, 10]

Attempts have, therefore, been directed by various workers [3–5] to separate the main constituents of oil in chromatographic papers prior to fluorescence studies, using different solvents for identification. The success of such methods obviously depends upon the relative proportions of the different constituents in an oil sample, as well as upon the efficiency of the separations, particularly of the different molecular weight resin units. Although, in a rigid sense, detection of asphaltenes in an oil sample should be considered as a more sure test for distinguishing a crude oil, fluorescent colours such as orange and/or brown, exhibited by heavier resin molecules, may be taken as sufficient for the purpose, since some crude oils of low specific gravities (0·78–0·79) have been found to contain practically no asphaltenes, although resins could be detected.

Experience has shown that identification of crude oils, particularly those containing too small a proportion of " short residue " from well cuttings, cores, or drilling muds, poses a great problem, as only blue and yellow fluorescent zones are shown by the conventional chromatographic methods [3–5] reported in the literature. Identification of traces of crude oils from such well samples becomes all the more problematical when wells are drilled with oil emulsion mud or water-base mud, spotted with diesel oil, and the hot water technique,[6] as reported, is a poor answer to such problems where crude oil is highly diluted with diesel oils. Thus a new approach for solving such problems is a pressing demand in oil exploration activities.

Of the main constituents of crude oils, ethyl acetate can easily dissolve oily components and light resins, while heavy resins are dissolved on prolonged refluxing. This solvent has been used for separating asphaltenes from other constituents of crude oils for geochemical characterization by M. Louis [7] *et al.* Therefore, if

* MS received 4 November 1960.

† Oil and Natural Gas Commission, Dehra Dun, India.

properly manipulated, ethyl acetate can completely separate oily components and light resins from a drop of test sample spotted on a filter paper, leaving behind at the centre asphaltenes and heavy resins which can be identified by the clear orange or brown fluorescent colours. In the present paper, techniques of identifying traces of crude oils from different well samples using ethyl acetate as a developing solvent have been described. Preliminary concentration of the " short residues " which contain all the resins and asphaltenes of crude oils are sometimes necessary, particularly when the test sample is a very light crude oil and/or diluted with diesel oil.

EXPERIMENTAL

G. R. E. Merck solvents and Whatman No. 1 filter papers are used throughout the experiments. Fluorescence is studied with the Model IC fluorometer of Rotary Engineering Co., Midland, Texas, having a mercury vapour lamp as the ultra-violet source.

(1) *Identification of Traces of Crude Oil from Well Cuttings, Cores, and Surface Rocks*

Procedure

(*a*) Powdered sample is dried at 105° C to completely remove moisture and any low boiling fractions of crude oils. This procedure, in a sense, concentrates the " short residue " of the oil.

(*b*) After complete extraction of the soluble matter with chloroform from the dried sample, the extract is filtered or centrifuged to remove suspended particles which would otherwise interfere with subsequent fluorescence studies.

(*c*) The clear extract is evaporated over a water bath until no smell of chloroform can be detected, when only the extracted soluble matter is left behind.

(*d*) A drop of the extracted matter is transferred carefully to the centre of a filter paper previously wetted with ethyl acetate, and before it can dry up, more ethyl acetate is allowed to run on dropwise to wash the material until no further washable matter remains at the centre.

If the extracted material is semi-solid or solid, prior wetting with ethyl acetate will help in transferring it to the filter paper.

(*e*) The developed chromatogram of any drop of crude oil when viewed under ultra-violet light shows a clear orange or brown spot at the centre with blue and yellow zones moved far off.

(*f*) If washing with ethyl acetate leaves the centre free of any coloured fluorescent spot or dark spot, further concentration of the " short residue " in the extracted material is needed prior to development of the chromatogram.

The extracted material is well mixed with excess of ethyl acetate and allowed to stand for a few hours. The solution is filtered and the trace quantity of the residue that adheres to the filter paper and to the container is dissolved in chloroform. The chloroform solution is evaporated once again over the water bath to repeat the procedures (*d*) and (*e*).

The developed chromatogram of any crude oil will show a brown spot or dark spot turning deep brown on wetting with chloroform under ultra-violet light.

(*g*) Similar chromatograms made with extracts of cutch or lignites show either white or light yellowish white, while those of humus material show yellow or buff coloured central fluorescent spots.

(2) *Testing of Crude Oils*

Depending upon the nature of the crude oil, preliminary concentration of the " short residue " is needed for a successful test. It is, however, better to observe a general procedure of evaporating the low boiling fractions over a water bath for about an hour or so.

After concentration of the " short residue," one drop is put at the centre of a filter paper, previously wetted with ethyl acetate. Development of the chromatogram is made following procedures (*d*) and (*e*) of (1).

Results. Experimental results of several well cuttings, cores, and crude oil samples, obtained both by the proposed method and by the capillary method,[3] are incorporated in Table I.

(3) *Identification of Traces of Crude Oils in Drilling Muds, not Spotted with Diesel Oil*

(*a*) About 100–150 g of the sample is dried at 105° C for some time and crushed to powder.

(*b*) After complete extraction of the powdered sample with chloroform, the extract is filtered or centrifuged to remove any suspended matter.

(*c*) All other operations are similar to procedures (*c*)–(*f*) detailed in (1).

(4) *Identification of Traces of Crude Oils in Drilling Muds, Spotted with Diesel Oil*

Procedures laid down in (3) are sufficient for extraction of all the chloroform soluble materials from the above samples. As diesel oil dilutes the " short residue " of crude oils, if there be any, procedure (*f*) of (1) is needed for development of the chromatogram. If excess of crude oil be present, procedures (*d*) and (*e*) of (1) may be sufficient, while with excess of diesel oil in the mud, identification of crude oils will require special pre-treatments as detailed in (5).

(5) *Identification of Traces of Crude Oils in Diesel Oil Emulsion Mud*

(*a*) About 200 g of the emulsion mud is shaken with excess of acetone to separate the diesel oil and water from the mud. The acetone layer is decanted off to a

TABLE I

Sample No.	Nature of sample	No. of samples tested	Amount of chloroform soluble matter, %	Fluorescent colours by capillary method [2]	Fluorescent colours by the proposed method	Inference
1	2	3	4	5	6	7
1	Crude oil (light)	4 (from two different localities)	—	One sample—blue only Three samples—blue and yellow	All the samples—orange at the centre, blue and yellow extended zones	Proposed method but not the capillary method tests for crude oil
2	Crude oil	6 (from different localities)	—	Blue, yellow, brown zones	Brown at the centre, yellow and blue extended zones	Both the methods test for crude oil
3	Shale core samples previously flushed with chloroform to remove all soluble matter. Clean shale cores are mixed separately with three oil samples of sample No. 2 to give approx 0·01% of oil	3	Soluble matter as found is between 0·007–0·008%	Blue and yellow	Brown at the centre, yellow and blue extended zones	Proposed method but not the capillary method tests for crude oil
4	Sandstone cores previously flushed with chloroform to remove all soluble matter. Clean sandstones are mixed separately with two oil samples of sample No. 1 to give approx 0·04% of oil	2	Soluble matter as found is between 0·009–0·01	Blue and very light yellow	Light orange at centre, yellow and blue extended zones	Proposed method but not the capillary method tests for crude oil
5	Shale and claystone cores of six oil wells, from horizons proved to contain oil in them	40	Between 0·05–0·001	Blue and yellow zones	Orange at the centre and yellow and blue extended zones	Proposed method but not the capillary method detects oil in the samples
6	Shale cores of few oil wells from horizons proved to contain oil	40	Between 0·15–0·02	Blue, yellow, and brown zones	Brown at the centre and yellow and blue extended zones	Both the methods detect oil in samples
7	Well cuttings from several oil wells from horizons proved to contain oil or near to those promising zones	12	Between 0·01–0·002	In only two cases blue, yellow, and brown zones; in others blue and yellow zones	Orange and/or brown at the centre and yellow and blue extended zones	All the samples contain oil, proved by the proposed method
8	Lignites	4	Between 0·004–0·0003	Blue and yellow zones	Practically nothing or very light yellowish white spot at the centre and blue and yellow extended zones	Proposed method not the capillary method confirms absence of oil
9	Cutch	2	About 0·002	Blue and yellow zones	Very light yellowish white spot at the centre, with blue and yellow extended zones	Proposed method but not the capillary method helps differentiation from crude oils
10	Humic acid and humus materials	3	0·15–0·08	Blue, yellow, and grey zones	Buff or yellow spot at the centre with yellow and whitish extended zones	Both methods help differentiation from crude oils

Some of the samples have been tested with paper partition chromatographic method,[4, 5] where in most cases only blue and yellow spots could be recognized under ultra-violet lampe.

TABLE II

Nature of samples	No. of samples tested	Amount of chloroform soluble matter, %	Fluorescent colours by capillary three analysis	Fluorescent colours by the proposed method	Inference
1	2	3	4	5	6
Water base drilling mud sample containing cutch, but no crude oil	2	0·0002–0·0005	Blue and yellow zones	Practically nothing at the centre. Blue and yellow extended zones	Proposed method confirms absence of crude oil
Above mud sample containing 0·005–0·05% crude oil by weight	4	0·008–0·07	In three cases blue and yellow zones, while in the fourth, blue, yellow, and brown zones	Orange or brown at the centre with blue and yellow extended zones in all the samples	Proposed method but not the capillary method tests for crude oil in all the samples
Above mud containing crude oil mixed with 1–2% of diesel oil	3	—	In all these cases blue zones only	Brown at the centre with blue and yellow extended zones	Proposed method but not the capillary method tests for crude oil
Oil emulsion mud made with 20% diesel oil by volume, but not containing any crude oil	1	—	Blue zone only	Nothing at the centre and light blue and light yellow extended zones	Does not give test for crude oil. Yellow zone is probably due to the cutch present in the mud
Above mud containing 0·005–0·05% crude oil by weight	4	—	Blue zone only	Brown at the centre with blue and yellow extended zones	The proposed method but not the capillary method tests for crude oil

Some of the samples are tested also with paper partition method,[4, 5] where in most cases only blue and yellow spots could be recognized under ultra-violet.

separate container. The process is repeated two or three times to collect almost completely all the diesel oil and water. The mud thus remaining is dried to 105° C. The acetone solution is heated over a water bath with occasional stirring to drive off acetone and water. The dried mud is exhaustively extracted with chloroform and the chloroform extract is mixed with the oil left after evaporation of acetone. The whole solution is diluted with chloroform and filtered.

It is difficult to remove all water from the emulsion mud by direct heating at 105° C, since diesel oil separates and forms a protective layer at the top. Extraction of diesel oil and water from the emulsion mud with acetone obviates this difficulty.

(*b*) The clear chloroform solution is heated over a water bath to remove all chloroform.

(*c*) The diesel oil, together with the extracted material, is distilled in a micro-distillation apparatus at 10 mm pressure of mercury, when all diesel oil, together with the distillate fractions of the crude oil, is removed, leaving the traces of the crude oil residue. Distillation is carried out carefully, avoiding any cracking.

(*d*) The chromatogram of the crude oil residue is developed according to the procedure (*d*)–(*f*) of (1).

Results. Table II contains the results of the investigation carried out with known amounts of crude oils in water base mud and in a diesel oil emulsion mud containing 20 per cent diesel oil by weight.

Discussion

(*a*) Data incorporated in Tables I and II show that the proposed method can detect traces of crude oil in all types of samples, provided extraction of the oil therefrom is complete. As it is difficult to extract oil with chloroform from water wet clays or sands, drying of the sample ensures better extraction.

(*b*) The limit of detection depends upon the nature of the crude oil. An oil containing a high percentage of " short residue " can be detected to a much lower concentration than light oil having a very low content of " short residue."

(*c*) Prior concentration of " short residue " helps in transferring more of the resins and asphaltenes to the spot and it is a definite advantage to obtain a clear chromatogram, as the success of the test lies in the detection of fluorescent colours of the heavy resins and/or of the asphaltenes.

(*d*) As traces of chloroform in the test drop of the extract will help the spreading of even the heavy resins and asphaltenes on the filter paper, careful elimination of chloroform from the extract is needed.

(*e*) Once the oil drop is allowed to dry up on the filter paper, it is difficult to wash down even the light resins with the solvent and so spotting over ethyl acetate wet paper and development of the chromatogram before the oil drop dries up is essential. This procedure helps in washing oily components and light resins easily, while heavy resins and asphaltenes become precipitated and remain at the spot.

(*f*) Blank vacuum distillation carried out with diesel oil only shows that no resins or asphaltenes are formed from diesel oil during the operation. But since commercial diesel oil contains some additives, which might interfere in the identification of traces of crude oil, it is advantageous to run the blanks with the same diesel oil used to prepare the emulsion mud, side by side, while identifying traces of oil in emulsion mud itself.

(*g*) Of all the interfering substances, such as extracts of cutch (quebracho), lignites, and humus materials, etc., the chromatogram obtained from the latter may cause confusion in certain cases if careful observation is not made. The central spot of the chromatogram of the extract of the humus materials is either yellow or buff in colour under ultra-violet light, while that of the crude oil is orange and/or brown. Any confusion arising between buff and brown fluorescent spots can be cleared up by wetting the spot with a drop of chloroform when the buff coloured spot given by extracts of humus materials turns dull yellow, while the brown spot of crude oil turns deeper brown, obviously due to deep brown colour contributed by the wetted asphaltenes, present along with the heavy resins at the spot.

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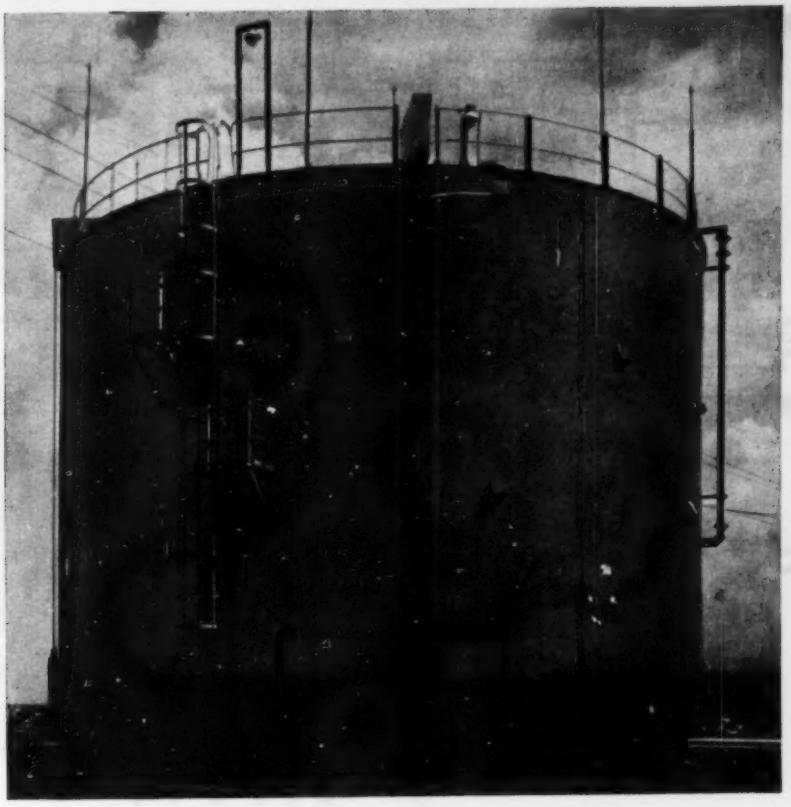

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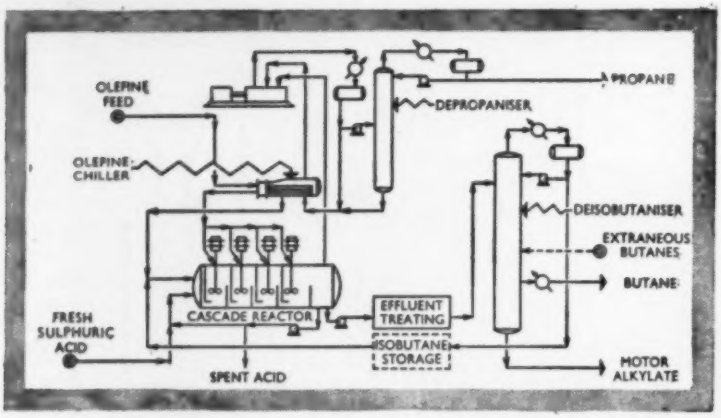

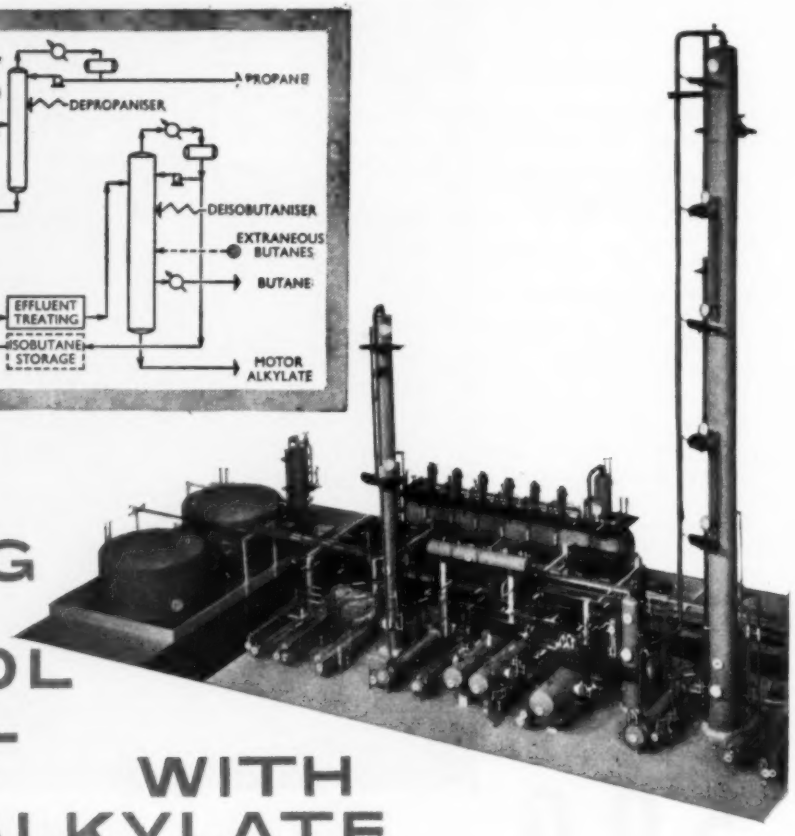

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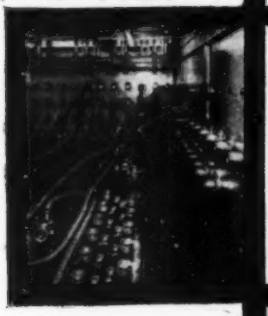

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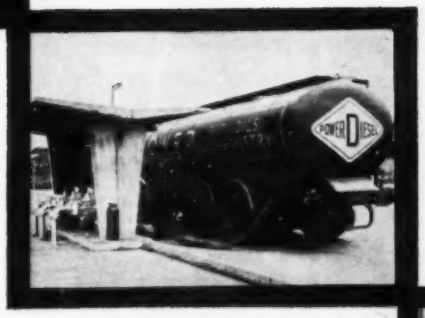

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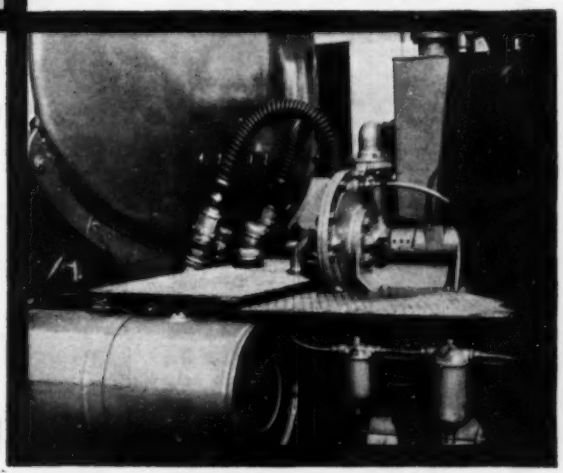

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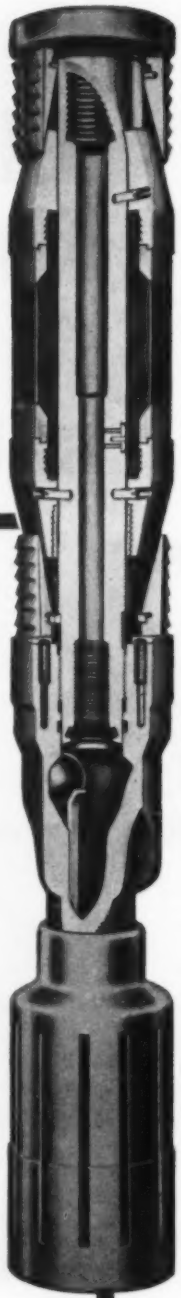

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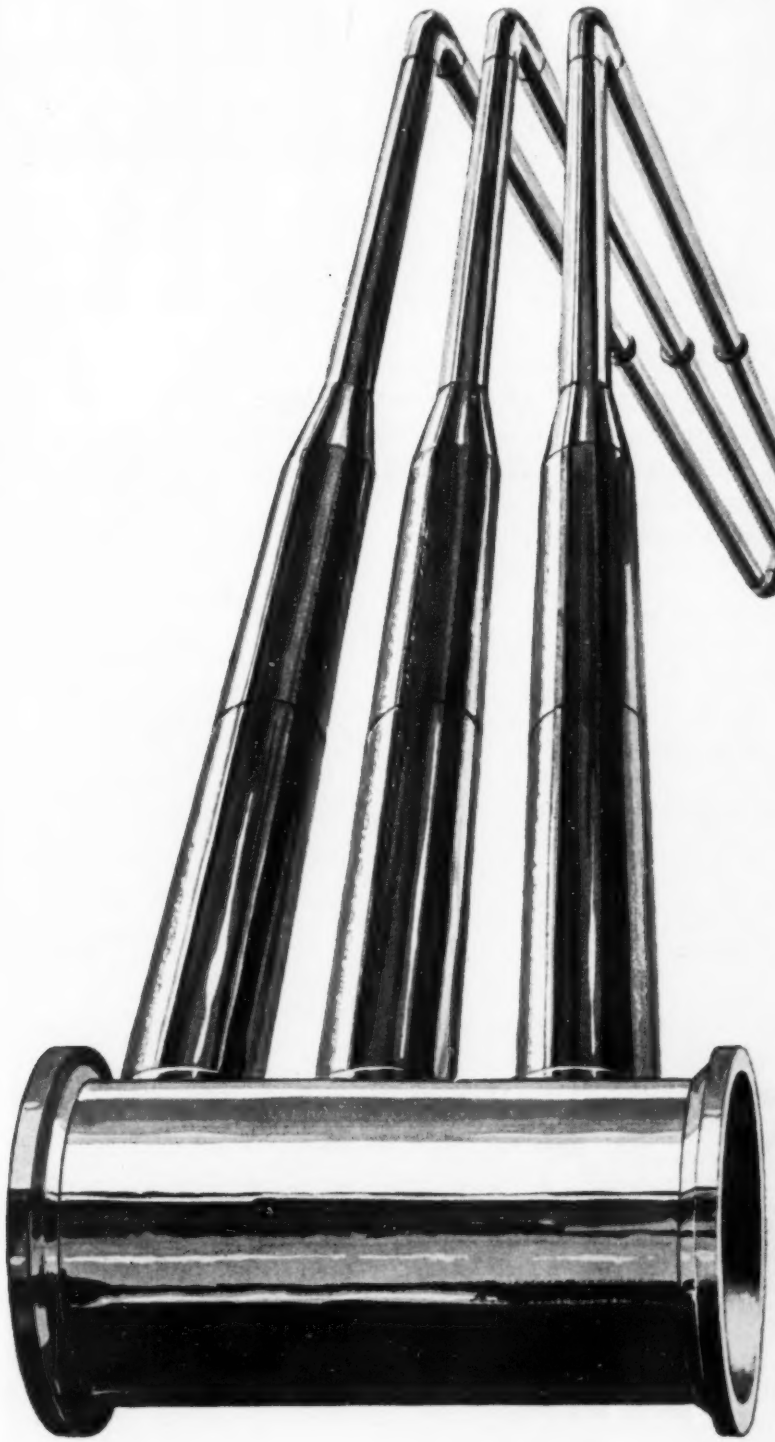

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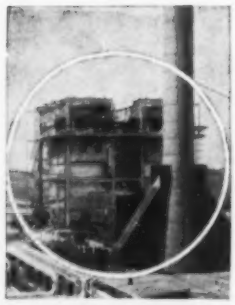

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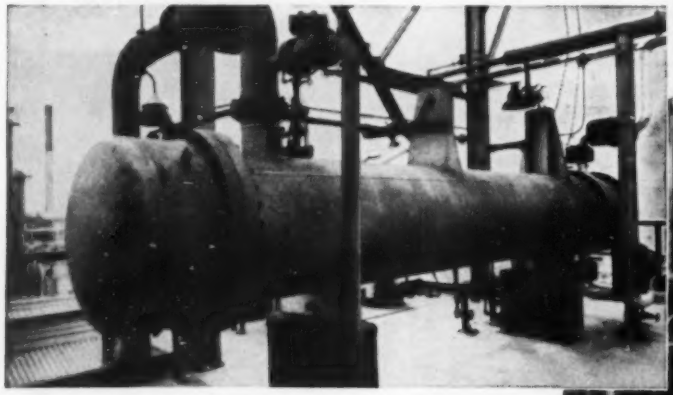

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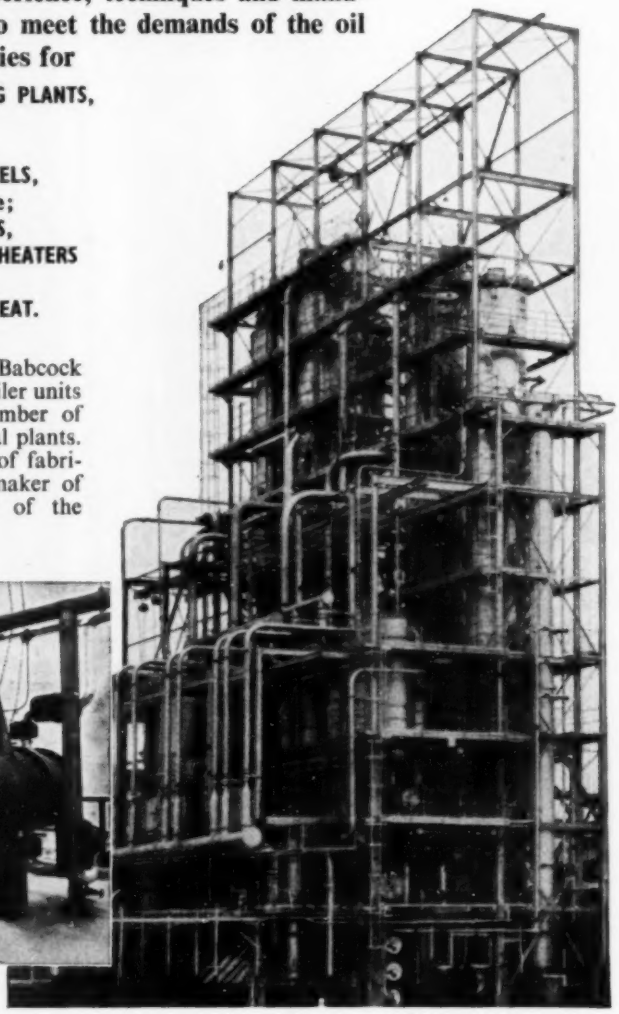

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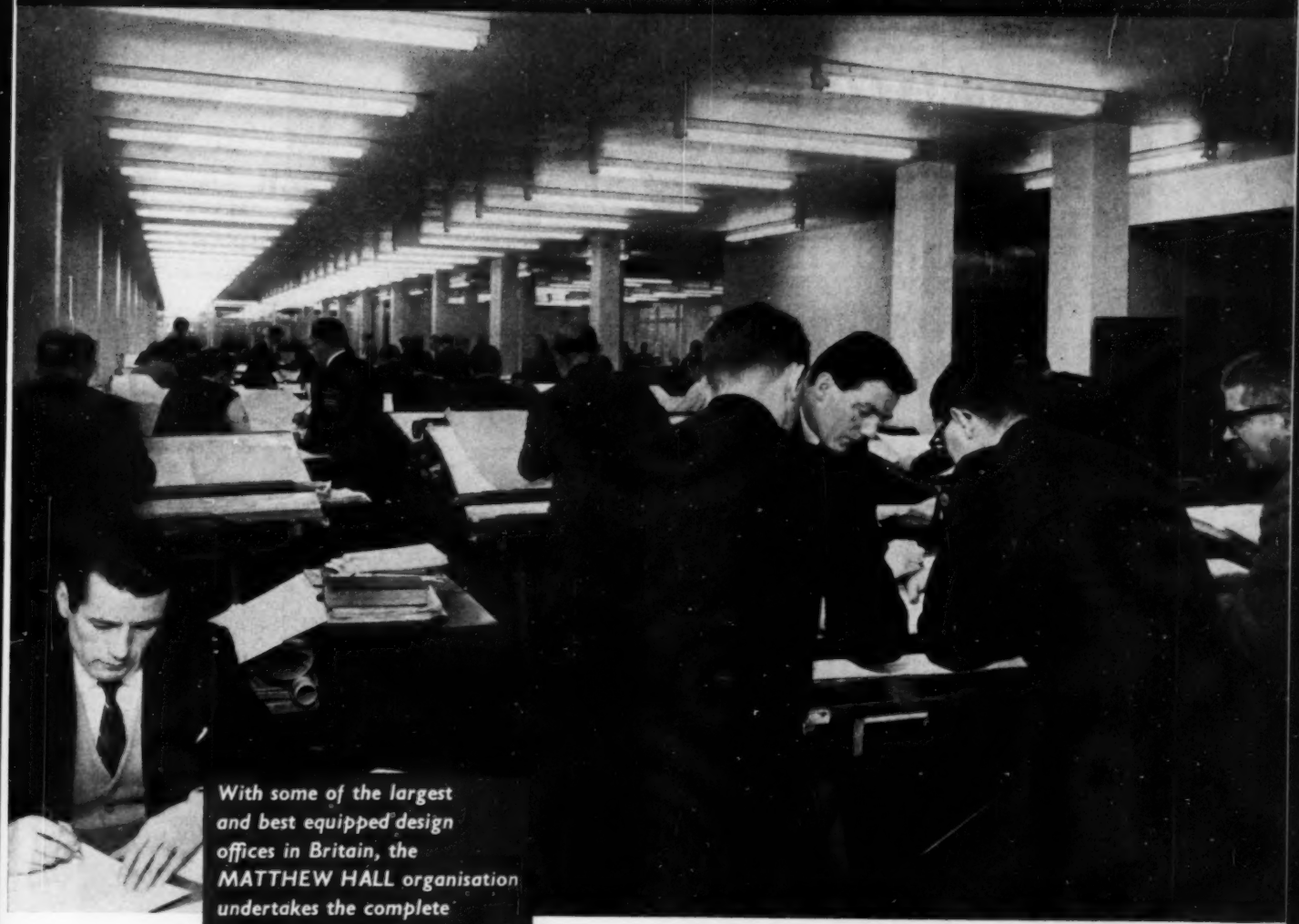

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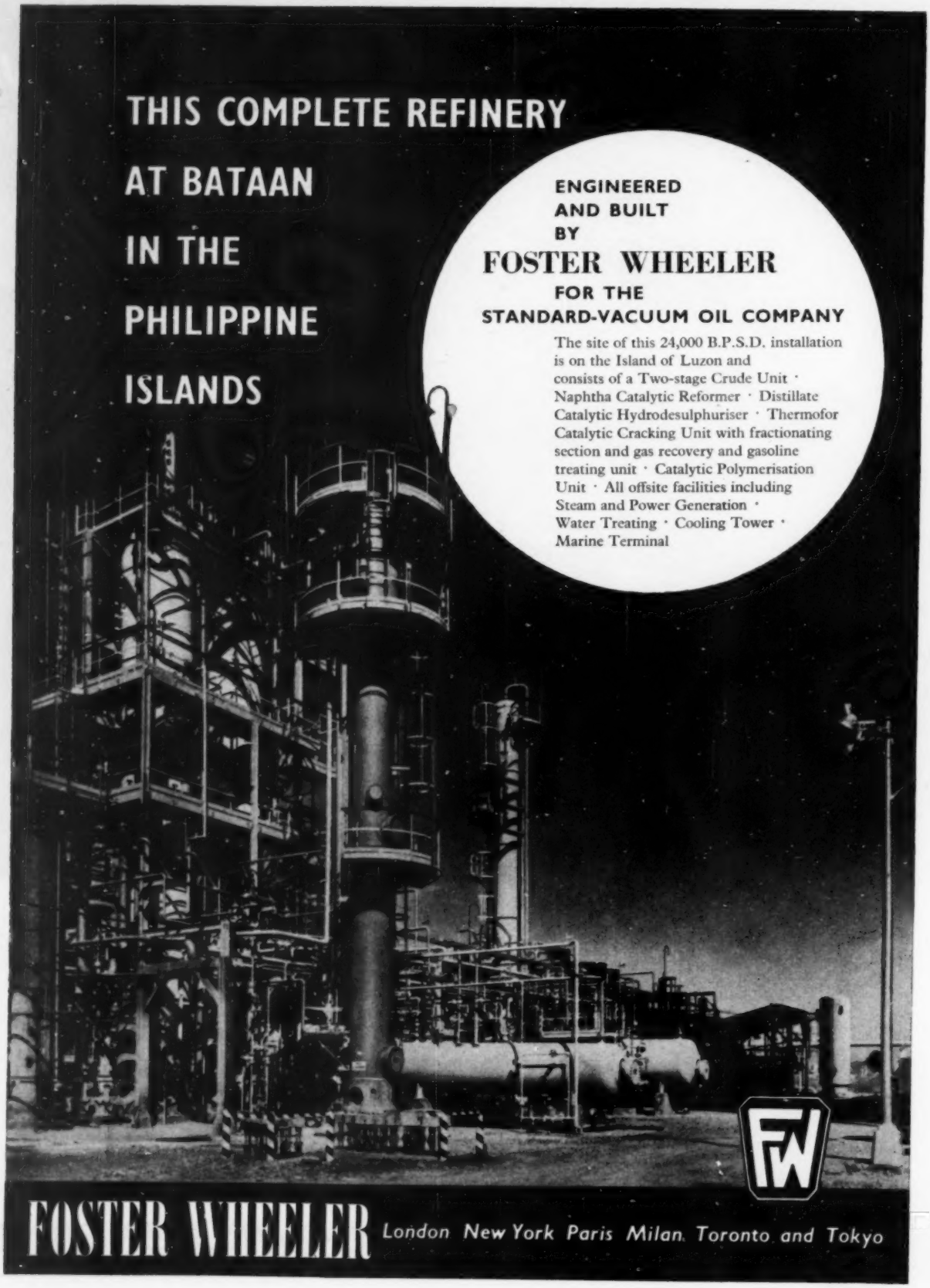
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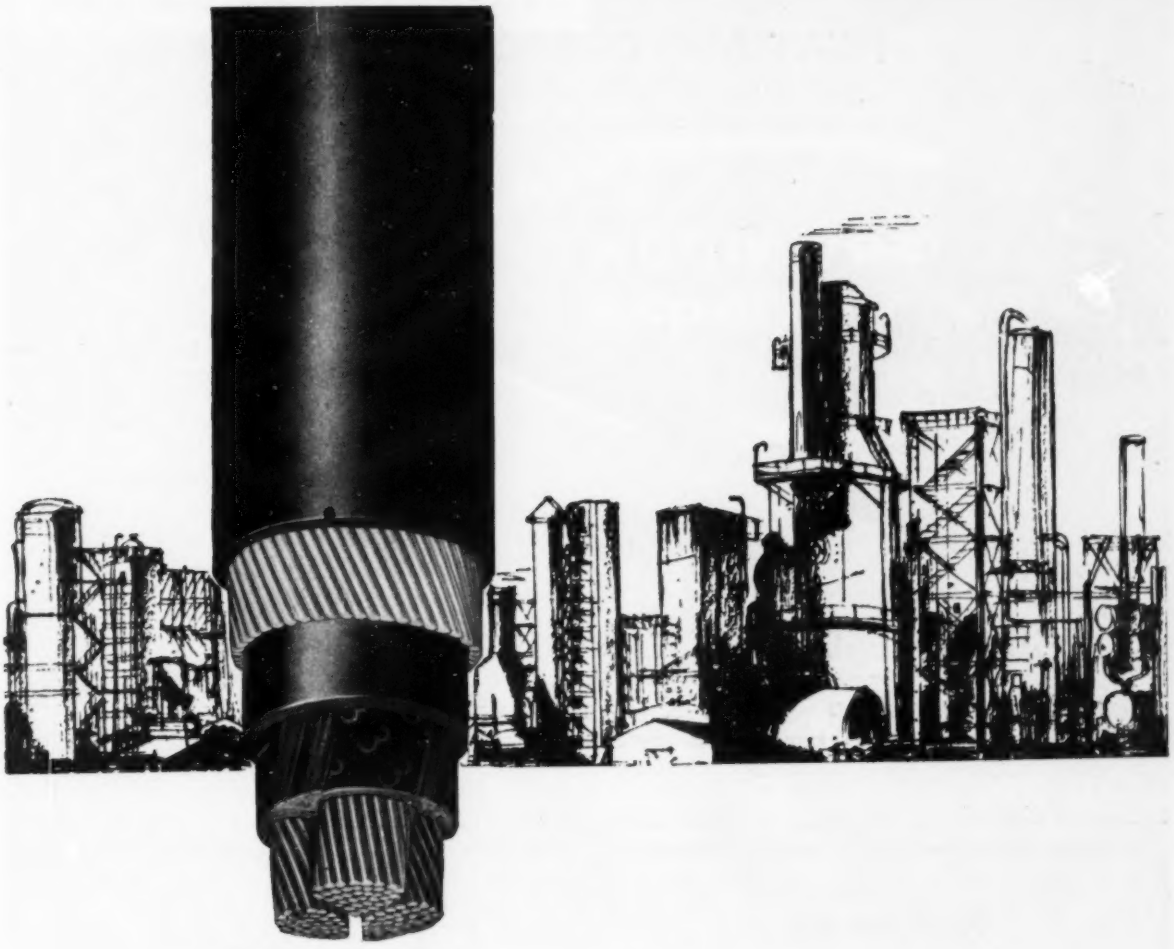

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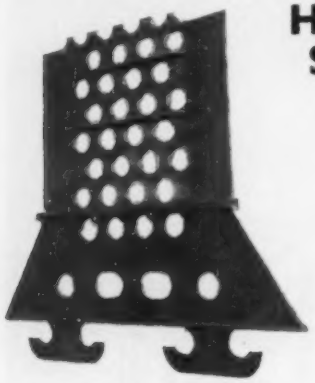

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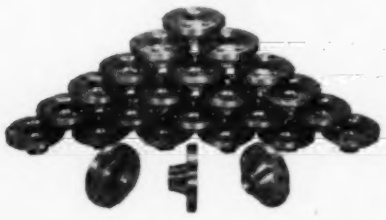

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The picture shows work on the rotor of an L21C gas turbine being built for the Basrah Petroleum Co. Larger machines of similar design—the L51C—were recently installed in Iran to supply power for the electrification of the Gach Saran oilfield.

For further information write to the AEI Turbine-Generator Division at Trafford Park, Manchester 17, or to your local AEI office.

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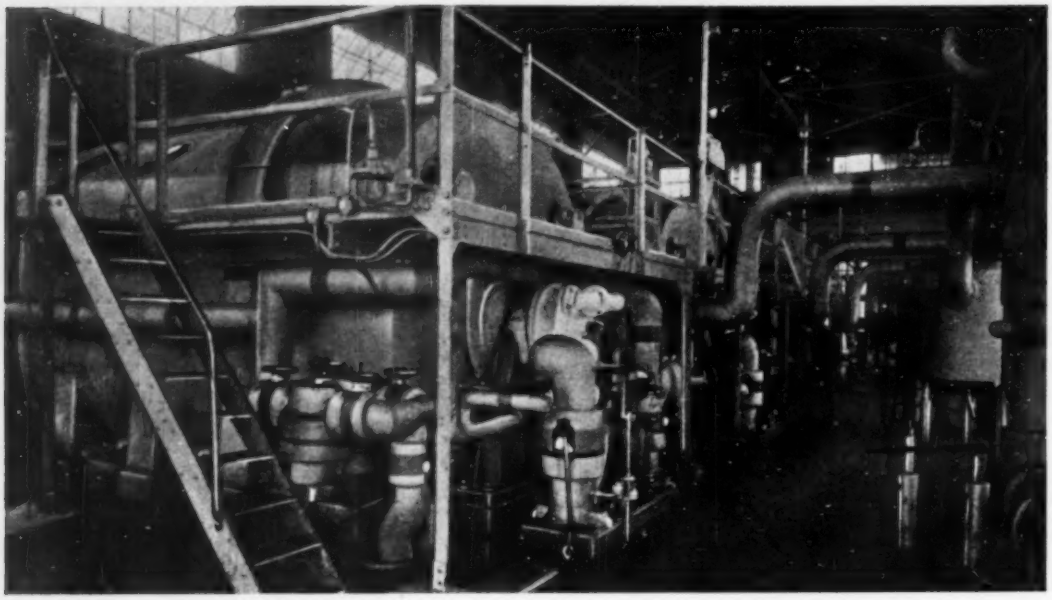

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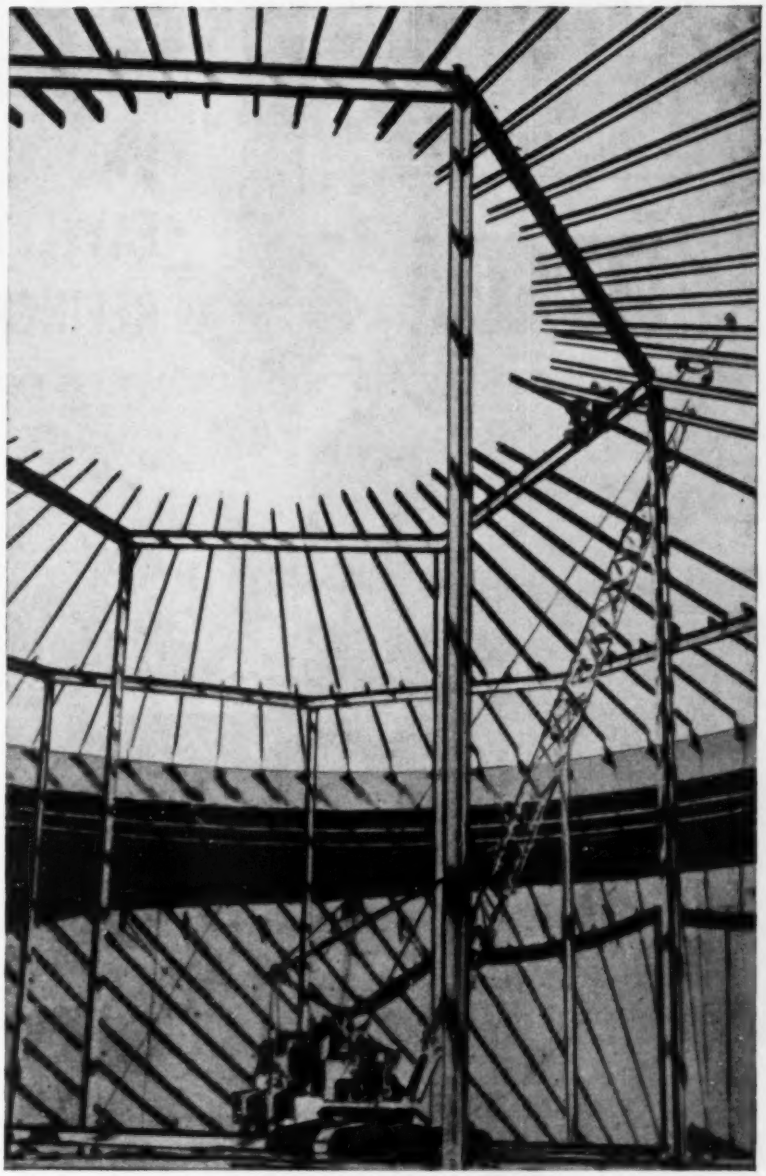

This lattice work of roof trusses over an oil storage tank is symbolic of the interlinked skills and techniques which Mechans bring to every tankage project.

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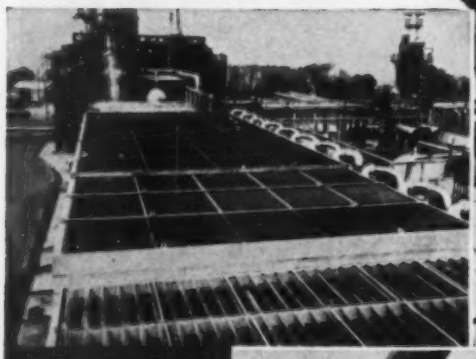

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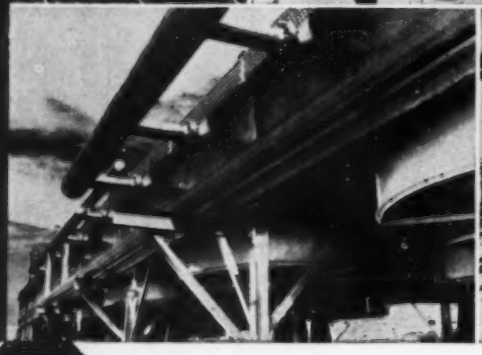
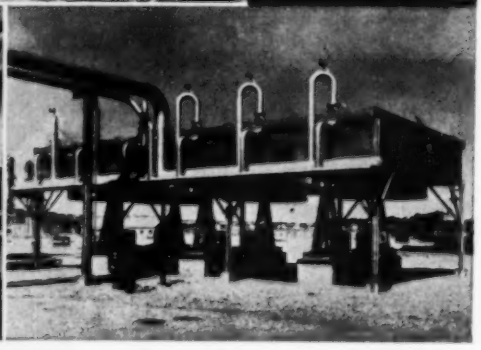
FAWLEY





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